Photograph (front cover) Westward view of Cache Creek from the bridge at Rumsey, California, by Cathy Munday, U.S. Geological Survey.

Mercury and Methylmercury Concentrations and Loads in the Cache Creek Basin, California, January 2000 through May 2001

By Joseph L. Domagalski, Charles N. Alpers, Darell G. Slotton, Thomas H. Suchanek, and Shaun M. Ayers

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Conversion Factors

Multiply	By	To obtain
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
gram (g)	0.03527	ounce (oz)
gram per day (g/d)	0.03527	ounce per day (oz/d)
square kilometer (km^2)	0.3861	square mile (mi^2)
liter (L)	1.057	quart (qt)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=1.8\ °C+32.$$

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Concentrations of chemical constituents in water are given either in nanograms per liter (ng/L) or micrograms per liter (µg/L).

Acronyms and Abbreviations

Al, aluminum

B, boron

BMSL, Battelle Marine Sciences Laboratory

Cl, chloride

CO_2, carbon dioxide

DOC, dissolved organic carbon

DI, deionized

DL, detection limit

δD, delta deuterium, $^2H/^1H$ relative to Vienna Standard Mean Ocean Water

^1H, hydrogen-1

^2H, hydrogen-2, deuterium

H_2, elemental hydrogen

Hg, mercury

HgS, cinnabar

Hg (II), ionized, divalent mercury

Li, lithium

^{16}O, oxygen-16

^{18}O, oxygen-18

$\delta^{18}O$, delta oxygen-18, $^{18}O/^{16}O$ relative to Vienna Standard Mean Ocean Water

p, level of significance

per mil, per thousand

ppm, parts per million

R^2, coefficient of determination

RPD, relative percent difference

SO_4, sulfate

UCD, University of California at Davis

USGS, U.S. Geological Survey

VSMOW, Vienna Standard Mean Ocean Water

µm, micrometer

mL, milliliter

ng, nanogram

>, greater than indicated value

<, less than indicated value

Mercury and Methylmercury Concentrations and Loads in the Cache Creek Basin, California, January 2000 through May 2001

By Joseph L. Domagalski[1], Charles N. Alpers[1], Darell G. Slotton[2], Thomas H. Suchanek[3] , and Shaun M. Ayers[2]

Abstract

Concentrations and mass loads of total mercury and methylmercury in streams draining abandoned mercury mines and near geothermal discharge in the Cache Creek Basin, California, were measured during a 17-month period from January 2000 through May 2001. Rainfall and runoff averages during the study period were lower than long-term averages. Mass loads of mercury and methylmercury from upstream sources to downstream receiving waters, such as San Francisco Bay, were generally the highest during or after winter rainfall events. During the study period, mass loads of mercury and methylmercury from geothermal sources tended to be greater than those from abandoned mining areas because of a lack of large precipitation events capable of mobilizing significant amounts of either mercury-laden sediment or dissolved mercury and methylmercury from mine waste. Streambed sediments of Cache Creek are a source of mercury and methylmercury to downstream receiving bodies of water such as the Delta of the San Joaquin and Sacramento Rivers. Much of the mercury in these sediments was deposited over the last 150 years by erosion and stream discharge from abandoned mines or by continuous discharges from geothermal areas. Several geochemical constituents were useful as natural tracers for mining and geothermal areas. These constituents included aqueous concentrations of boron, chloride, lithium, and sulfate, and the stable isotopes of hydrogen and oxygen in water. Stable isotopes of water in areas draining geothermal discharges were enriched with more oxygen-18 relative to oxygen-16 than meteoric waters, whereas the stable isotopes of water from much of the runoff from abandoned mines were similar to that of meteoric water. Geochemical signatures from stable isotopes and trace-element concentrations may be useful as tracers of total mercury or methylmercury from specific locations; however, mercury and methylmercury are not conservatively transported. A distinct mixing trend of trace elements and stable isotopes of hydrogen and oxygen from geothermal waters was apparent in Sulphur Creek and lower Bear Creek (tributaries to Cache Creek), but the signals are lost upon mixing with Cache Creek because of dilution.

Introduction

The Cache Creek Basin, also known as the Cache Creek watershed or drainage basin (fig. 1), is an important source of total inorganic mercury to downstream areas including the San Francisco Bay and the region known as the Delta of the Sacramento and San Joaquin Rivers (Domagalski, 1998, 2001; Foe and Croyle, 1999; Domagalski and Dileanis, 2000). Although the Cache Creek drainage basin covers only about 4 percent of the Sacramento River Basin, the mercury transported downstream can be as high as 50 percent of the total annual load of the Sacramento River Basin (Foe and Croyle, 1999). Sources of mercury within the Cache Creek drainage basin include natural geothermal springs, and abandoned and inactive mercury mines (fig. 1). Sulphur Creek has several active geothermal springs within its drainage.

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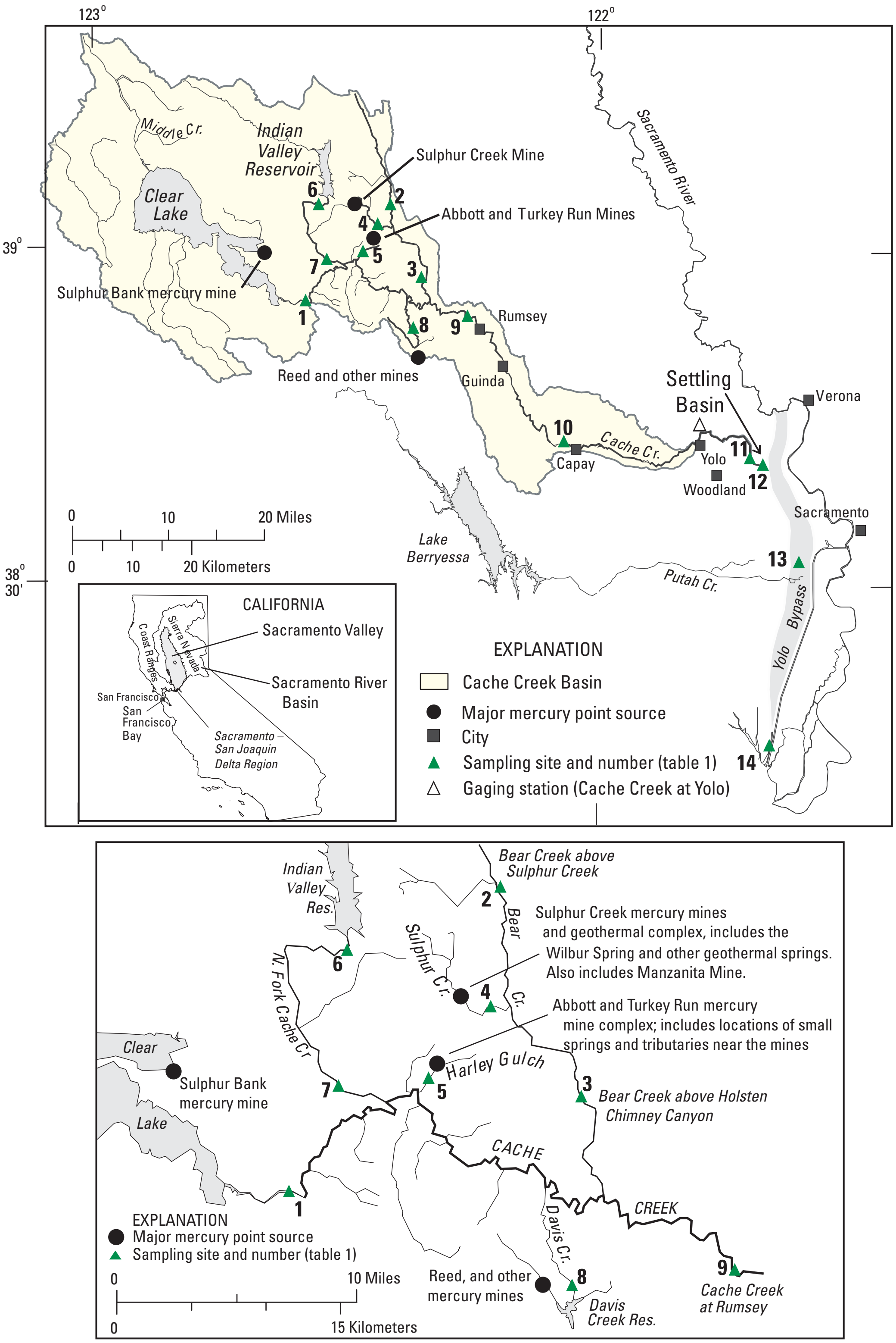

Figure 1. Study area and location of sampling sites and major mercury point sources, Cache Creek Basin, California. Cr., Creek; N., North; Res., Reservoir.

Following the discovery in 1848 of placer gold in the California Sierra Nevada, mercury production was especially high in the Coast Ranges of California. Cenozoic-age cinnabar (HgS) hydrothermal mercury deposits were mined at several locations in the Cache Creek Basin, including areas near Clear Lake and within the Cache Creek and Putah Creek drainages (Rytuba, 1996). The Clear Lake deposits are the northernmost part of a group of similar deposits associated with volcanism and migration of a transform fault system within the central part of the Coast Ranges region of California (Rytuba, 1996). Peak production of mercury occurred in 1877 when mines of the California Coast Ranges produced approximately 2,776 metric tons of elemental mercury (Bradley, 1918). This elemental mercury was transported out of the Cache Creek Basin and used to mine gold at other locations in California and Nevada, and around the Pacific Rim, but residues from the abandoned mercury mines remain a source of total mercury to Cache Creek and downstream receiving bodies of water (Domagalski, 1998; Foe and Croyle, 1999). Mining wastes enter streams primarily through runoff associated with rain, and the highest observed concentrations of total mercury in Cache Creek have followed rainfall events (Domagalski, 1998, 2001). Mercury from geothermal sources enters the creeks year-round; however, most of the annual load of total mercury is transported from the Cache Creek Basin during the 4-month period of high rainfall (December through March) (Domagalski, 1998; Foe and Croyle, 1999).

The mercury transported from the Cache Creek Basin to receiving waters may pose a human health problem if it enters the aquatic food web and methylmercury eventually bioaccumulates in fish to levels above health guidelines. Although some of the inorganic or total mercury can bioaccumulate in fish, the organic form, methylmercury, is more likely to do so (Zilloux and others, 1993). Although the processes that produce methylmercury in a given ecosystem are not completely understood, one step is associated with bacteria in anoxic sedimentary environments, especially during the chemical reduction of sulfate to sulfide (Compeau and Bartha, 1985; Gilmour and others, 1992). Other bacteria are known to detoxify the methylmercury by breaking the chemical bond of the methyl group to the mercury ion, a process referred to as demethylation (Marvin-DiPasquale and others, 2000). Methylmercury can also be degraded by sunlight, a process known as photo-degradation. When the rate of mercury methylation exceeds the rate of demethylation, methylmercury may bioaccumulate.

The potential for the mercury of the Cache Creek Basin to change to the methylated form, either within the Cache Creek Basin or when transported downstream to a receiving body of water such as the Delta, is largely unknown. Most of the mercury transported through Cache Creek is presumably in the form of cinnabar or metacinnabar as a suspended solid. The cinnabar or metacinnabar must dissolve or oxidize to liberate aqueous ionized mercury, Hg (II), before the mercury can be transformed to methylmercury. Although previous studies (Foe and Croyle, 1999; Domagalski, 2001) have documented the amount of total mercury transported from the Cache Creek Basin, the present study is the first to document the fraction of mercury present as methylmercury at different locations within the Basin.

Purpose and Scope

The primary purpose of this report is to present the concentrations and mass loads of mercury and methylmercury for selected surface water sites in the Cache Creek drainage basin during January 2000 through May 2001, to relate the loads to sources of mercury and methylmercury, and to explain the seasonal variation in concentrations and mass loads. The report also provides chemical data for mercury and methylmercury, for selected trace elements, and for stable isotopes of hydrogen and oxygen in water molecules within the Cache Creek drainage basin for the same time period.

The report provides data and interpretations for part of a larger study, funded by the CALFED Bay–Delta Program, of the impact of mercury in the Bay–Delta drainage basin on ecology and human health (http://loer.tamug.tamu.edu/calfed/). The larger investigation is examining mercury bioaccumulation, the potential for mine remediation within the Cache Creek drainage basin to reduce mercury loads, and issues associated with ecosystem restoration within the Delta of the Sacramento and San Joaquin Rivers.

Acknowledgments

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Description of Study area and Selection of Sampling Sites

The Cache Creek Basin occupies approximately 3,000 square kilometers in northern California (fig. 1). The area upstream of Rumsey is characterized by the low hills of the California Coast Ranges, whereas the area downstream of Rumsey is part of the Sacramento Valley. Land cover in the upstream portion of the basin is mainly forest and grazing land with minor amounts of orchards and cropland. The amount of land used for crops increases downstream of Rumsey. Former mine sites represent a relatively small amount of the total land cover.

Cache Creek begins as outflow from Clear Lake. The largest tributary to Cache Creek, the North Fork Cache Creek, originates in the northern part of the basin and includes the Indian Valley Reservoir. Flows of the North Fork Cache Creek below Indian Valley Reservoir are partly controlled by reservoir releases. Another major tributary to Cache Creek is Bear Creek, which does not have a reservoir within its drainage area. Both Clear Lake and Indian Valley Reservoir are used, in part, to supply irrigation water to farmers in the lower parts of the Cache Creek Basin. During summer, flows in Cache Creek and North Fork Cache Creek are entirely managed for irrigation, and essentially no water reaches the Sacramento River until winter (Domagalski and others, 2000).

There are numerous smaller tributaries to Cache Creek; some drain geothermal areas or abandoned mine sites. Harley Gulch (fig. 1) drains an abandoned mercury mine complex (the Abbott and Turkey Run Mines). Davis Creek drains an area including the Reed Mine, which was remediated by the Homestake Mining Company in conjunction with their development of the McLaughlin gold mine. Davis Creek Reservoir is a small reservoir on Davis Creek. The Sulphur Creek drainage includes natural sources of mercury from geothermal springs and some mine wastes, including wastes from mercury and gold mines. Sulphur Creek drains into Bear Creek, a tributary to Cache Creek above Rumsey.

Irrigation-period flows of Cache Creek (fig. 1) are managed to deliver only the amount of water purchased by local farmers for consumptive irrigation use. As a result, very little water leaves the basin during the irrigation season. Fall and winter flows tend to be low, at least initially, because releases from Clear Lake and Indian Valley Reservoir are very low. Seasonal rainfall causes high flows in winter. In addition, the level of Clear Lake or Indian Valley Reservoir is occasionally lowered for flood protection during the winter rainy season, generally December through March. Water from Cache Creek that leaves the basin enters a flood-control channel of the Sacramento River system known as the Yolo Bypass (fig. 1). Water from the Sacramento River also discharges into the Yolo Bypass through a weir when the Sacramento River near Verona exceeds 1,560 m^3/s. The flood control system is designed to reduce the potential for flooding in downstream areas, especially in the city of Sacramento. The Yolo Bypass rejoins the Sacramento River downstream in the Delta region. The Yolo Bypass region is almost entirely crop land; a smaller amount is wildlife habitat.

Sampling sites were selected to assess representative locations of potential sources of mercury within the Cache Creek drainage basin. Stream sites immediately downstream of the dams on both Clear Lake and Indian Valley Reservoir were sampled to determine mercury and methylmercury concentrations from either the lake or the reservoir. Another sampling site was on the North Fork Cache Creek just upstream of its confluence with Cache Creek. Sites on small tributaries or other water bodies near mercury mines or natural mercury sources included two sites on Bear Creek (an upper site, Bear Creek above Sulphur Creek, and a lower site, Bear Creek above Holsten Chimney Canyon) and one site each on Sulphur Creek (which receives runoff from geothermal springs), Harley Gulch (downstream of the Abbott and Turkey Run Mines), and Davis Creek Reservoir at its spillway. Additional sites on Cache Creek included a site at Rumsey, which is centrally located in the Cache Creek Basin, and two sites just upstream of the point where Cache Creek discharges into the Yolo Bypass; these latter two sites surround an area known as the Cache Creek Settling Basin, which is designed to trap sediment transported out of the Cache Creek drainage basin. Finally, two sites were in the Yolo Bypass: one in the central portion of the Yolo Bypass (Yolo Bypass at Interstate 80 near West Sacramento) and the second site (Lower Yolo Bypass) just upstream of where the Yolo Bypass discharges into the Delta region.

Methods

Some sites, including the Yolo Bypass sites and the site immediately downstream of the dam on Indian Valley Reservoir, were sampled only by the U.S. Geological Survey (USGS), and some sites, such as Bear Creek above Sulphur Creek and Cache Creek at Highway 505, were sampled only by the University of California at Davis (UCD). Other sites were sampled by both the USGS and UCD. Sampling sites are shown on figure 1 and listed in table 1. The frequency at which sites were sampled varied either because of hydrological conditions (such as low discharge) or logistical problems (difficult access or remote location). Water sampling by UCD was coupled with biological sampling of invertebrates and fish to assess mercury bioaccumulation (Slotton and others, 2004); UCD samples were timed to avoid peak storm event flows to best approximate average seasonal biotic exposure to mercury and methylmercury.

Table 1. Number, location, identification number, and name of sites sampled in Cache Creek Basin, California, January 2000 through May 2001

[Latitude and longitude are in degrees (°), minutes (′), and seconds (″). Site identification numbers are not available for sites that were sampled only by University of California at Davis; NA, not available]

Site number (see fig. 1)	Latitude	Longitude	USGS site identification number	Site name (abbreviated name, if any)
1	38° 55′ 27″	122° 33′ 53″	11451000	Cache Creek near Lower Lake (Clear Lake)
2	39° 05′ 50″	122° 25′ 12″	NA	Bear Creek above Sulphur Creek (upper Bear Creek)
3	38° 57′ 28″	122° 20′ 30″	11451715	Bear Creek above Holsten Chimney Canyon (lower Bear Creek)
4	39° 02′ 19″	122° 25′ 08″	11451690	Sulphur Creek at Wilbur Springs (Sulphur Creek)
5	39° 00′ 33″	122° 26′ 04″	11451540	Harley Gulch near Wilbur Springs (Harley Gulch)
6	39° 04′ 50″	122° 32′ 07″	11451300	North Fork Cache Creek near Clearlake Oaks (Indian Valley Reservoir)
7	39° 01′ 09″	122° 34′ 04″	11451500	North Fork Cache Creek at Highway 20
8	38° 51′ 51″	122° 21′ 11″	11451600	Davis Creek Reservoir at Dam, near Knoxville
9	38° 53′ 26″	122° 14′ 14″	11451800	Cache Creek at Rumsey
10	38° 41′ 47″	121° 57′ 12″	NA	Cache Creek at Highway 505
11	38° 43′ 40″	121° 43′ 44″	384340121434401	Cache Creek into Settling Basin
12	38° 40′ 40″	121° 40′ 23″	384040121402301	Cache Creek out of Settling Basin
13	38° 34′ 01″	121° 36′ 51″	11453120	Yolo Bypass at Interstate 80 near West Sacramento
14	38° 14′ 27″	121° 40′ 49″	381427121404901	Lower Yolo Bypass

In addition to the sites listed in table 1, the Abbott and Turkey Run and the Sulphur Creek mine site areas were sampled in more detail by a separate team from UCD. The locations of several sampling sites in these areas are described in detail by Suchanek and others (2003). Splits of the UCD water samples from these locations were provided to the USGS for the analysis of inorganic constituents, as described in the next section.

Sampling and Sample Processing

Water samples were collected across the stream channel by the USGS using a USGS D-77 sampler designed for collecting isokinetic samples. Sampling protocols followed guidelines by Edwards and Glysson (1988), Ward and Harr (1990), Shelton (1994), and the U.S. Geological Survey (1999). The water samples were collected in 3-L Teflon bottles that had been rigorously cleaned for the purpose of collecting water samples for mercury and trace metals. The bottles were originally cleaned by immersion in 10-percent hydrochloric acid at 65 degrees Celsius for 3 days. After thorough rinsing with ultra-clean water, the bottles were tightly capped and double-wrapped in plastic for transport to field sites. After collecting a water sample, the bottles were rinsed with ultra-clean water and then cleaned in the field with a dilute detergent, followed by thorough rinsing with ultra-clean water, a rinse with 5-percent hydrochloric acid, and a final series of rinses with ultra-clean water. One set of sampling bottles was used only for sites influenced by geothermal sources or mercury mines expected to have high mercury concentrations, whereas another set was only used for downstream sites on the larger creeks and rivers expected to have low mercury concentrations. After collection, the water samples were composited in an 8-L Teflon-lined stainless-steel churn. The churn was cleaned by using dilute detergent followed by a thorough rinse with ultra-clean water, a thorough rinse with 5-percent hydrochloric acid, and a final series of rinses with ultra-clean water. Similar to the procedure for the 3-L Teflon sampling bottles, one churn was used only for sites influenced by geothermal sources or mercury mines, and a second churn was used only for the sites on the large creeks and rivers.

Water samples were taken from the churn for analyses of unfiltered water samples. Before filling the sample bottles, samples were churned for at least 1 minute to ensure that sediment was suspended uniformly. Samples were then collected for analysis of suspended sediment concentration, mercury and methylmercury in unfiltered water, trace elements in unfiltered water, nitrogen and phosphorus species in unfiltered water, measurement of pH and specific conductance, and oxygen and hydrogen isotope ratios in water. Samples were then preserved if required by the sampling protocol. A 0.45-µm high-capacity Gelman capsule filter was used for samples that were filtered as part of the sampling protocol. C-flex tubing (composed of a thermoplastic polymer) was used to pump the sample water through the filter. The tubing had been cleaned using detergent and rinsed with ultra-clean water. The tubing was then thoroughly rinsed by a peristaltic pump using 10-percent hydrochloric acid, followed by a final rinse with ultra-clean water. One set of tubing was dedicated for each site sampled. Before filtration, the capsule filter was rinsed by pumping 1 L of ultra-clean water through it. Then, a small amount of sample water was pumped through to displace the clean water. The filtration order for samples was total mercury, methylmercury, other trace metals, dissolved nitrogen and phosphorus species, and finally alkalinity. Samples to be analyzed (usually 50 ml) for dissolved and suspended organic carbon were processed using a 0.45-µm silver filter. The particles collected on the silver filter were analyzed for organic carbon to estimate suspended (particulate) organic carbon.

Water samples collected by UCD differed from those taken by the USGS in that the UCD samples were grab samples collected in the part of the river or stream judged to have the greatest discharge. The UCD group did not filter samples in the field, but rather transported the samples by overnight courier or ground transport to the laboratory where samples were immediately filtered and preserved. Samples taken for analysis of mercury and methylmercury were collected in 1-L pre-washed glass bottles supplied by the Battelle Marine Sciences Laboratory (BMSL). Samples taken for trace metals, alkalinity, and stable isotopes were collected in 4-L polyethylene bottles that were cleaned using the same procedure as that used for the Teflon-lined churns.

Analytical Methods

Samples collected by the USGS for the measurement of total mercury in water were analyzed according to the method of Roth (1994) at the USGS laboratory in Boulder, Colorado. This method uses cold vapor atomic fluorescence spectrometry. (Details of analytical chemical methodology are given by Puckett and van Buuren [2000].) Water samples collected by UCD also were analyzed using a cold vapor atomic fluorescence methodology at the BMSL in Sequim, Washington; complete details are given by Puckett and van Buuren (2000). The method is based on that of the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 1996). Methylmercury in water was measured using a similar method after distillation and ethylation of aqueous samples (Puckett and van Buuren, 2000). Both the USGS and UCD used the same methodology to analyze methylmercury at the BMSL. Selected major cations, iron, and silica in water were analyzed by inductively-coupled plasma atomic-emission spectroscopy (Alpers and others, 2000). Selected trace elements in water were analyzed by inductively-coupled plasma mass spectroscopy (Alpers and others, 2000). Nutrients were analyzed by the methods of Fishman and Friedman (1989) and Fishman (1993). Dissolved and suspended organic carbon were analyzed by the methods of Brenton and Arnett (1993).

Quality Assurance

A rigorous quality assurance program was adopted for this project. Full details of laboratory and field quality assurance requirements are given by Puckett and van Buuren (2000). Field-level quality assurance required at least one blank for every ten samples collected and at least one replicate for every ten samples.

Seven field blanks were collected for total mercury in unfiltered and filtered water during the three sampling events completed by the USGS. The concentrations of total mercury in unfiltered water blanks ranged from less than detection (0.5 ng/L) to 1.2 ng/L. The median value was 0.6 ng/L, which was estimated by setting the concentrations of non-detected values to one half the detection limit. The concentrations of total mercury in filtered blank samples ranged from less than detection (0.5 ng/L) to 1.2 ng/L. The median value was less than the detection limit. The concentrations of total mercury in environmental samples ranged from less than the detection limit to 3,070 ng/L, and 98 percent of all measured concentrations exceeded a concentration of 1 ng/L. Because these levels are much higher than those in blank samples, any contamination of the blanks was insignificant and does not affect the data set.

Six field blanks were collected for methylmercury in unfiltered and filtered water during the three sampling events completed by the USGS. Most of the measurements were less than the detection limit of 0.02 ng/L. Two samples of methylmercury in unfiltered water had concentrations just slightly above the detection limit, and the highest concentration was 0.03 ng/L. Bias caused by contamination was not significant and, therefore, does not affect the measurements of methylmercury in this data set.

All samples collected for total mercury in unfiltered and filtered water by the USGS were taken as replicates, and each of the replicate samples was analyzed three times. The median relative percent difference (RPD) for the values of total mercury in unfiltered water samples was 3.5 percent, whereas that for filtered water samples was 6.4 percent. The higher median RPD for the filtered water samples may be attributed to the lower concentrations of total mercury in filtered water. Six replicates were collected by the USGS for methylmercury analysis. The median RPD for methylmercury in unfiltered water samples was 8.5 percent, whereas that in filtered water was 4.5 percent. The filtered water samples do not provide a very good estimate of reproducibility because two of six replicate sets had methylmercury concentrations less than the detection limit.

The UCD sampling team also collected field blanks and replicates according to the quality assurance requirements (one each for every ten samples) specified by Puckett and van Buuren (2000). The median concentration for unfiltered water blanks was 0.32 ng/L for total mercury and less than the detection limit of 0.02 ng/L for methylmercury. The median concentration for the field blanks collected by the UCD team and filtered at the BMSL was 0.072 ng/L for total mercury and below the detection limit of 0.024 ng/L for methylmercury. The median RPD for replicate samples of total mercury in unfiltered water was 8.6 percent and that for methylmercury was 13.3 percent. The RPD for methylmercury in filtered water for the replicate samples collected by UCD was 7.5 percent and that for methylmercury was 20.1 percent. The higher RPD for methylmercury in filtered water samples used for the UCD data relative to the RPD for samples taken by the USGS (RPD of 4.5 percent) is probably due to more replicate pairs and to more replicate pairs having concentrations above the detection limit. Thus, the UCD data may provide a better indication of the replication of methylmercury in filtered water.

Additional information on quality assurance in this project is provided by the results of laboratory intercomparison studies. An intercomparison study with regard to analysis of total mercury in water by laboratories participating in the CALFED mercury project was an integral component of overall project quality-assurance oversight (van Buuren, 2002). This intercomparison study consisted of three rounds of testing in which participating laboratories were provided with splits of fresh-water and seawater samples that had been spiked with known concentrations of inorganic mercury. A total of three spiked seawater samples and four spiked fresh-water samples were prepared. The water samples were preserved with HCl, which causes a positive bias of 25 to 30 percent using the analytical method employed by the USGS laboratory in Boulder, Colorado. Without correcting for the bias introduced by the HCl preservative, results from the USGS laboratory were within a tolerance of three standard deviations (3-sigma) for four of the seven intercomparison samples; correcting the results from the USGS laboratory for the analytical bias introduced by the HCl preservative results in six of the seven samples falling within the 3-sigma tolerance. In addition, the USGS laboratory in Boulder has participated successfully in several round-robin comparisons of total mercury analysis conducted by the USGS Branch of Quality Assurance using Standard Reference Water Samples.

A separate laboratory quality assurance program was used to analyze oxygen and hydrogen isotope ratios for unfiltered water samples. Isotopic analyses of oxygen and hydrogen atoms in water are recorded as ratios relative to Vienna Standard Mean Ocean Water (VSMOW; O'Neil, 1986). Isotope ratios of oxygen, oxygen-18/oxygen-16 ($^{18}O/^{16}O$, expressed as $\delta^{18}O$ [delta oxygen-18]), and hydrogen, hydrogen-^{2}/hydrogen-1 ($^{2}H/^{1}H$, expressed as δD [delta deuterium]), in water were measured using a light stable isotope ratio mass spectrometer at the University of California, Davis, Department of Geology. $\delta^{18}O$ in carbon dioxide (CO_2) was measured after equilibration of the water at 25 degrees Celsius. Hydrogen isotope measurements were made on hydrogen gas (H_2) after reducing the water with zinc using a platinum catalyst. The calibration procedure used three unique standards; duplicates of each standard were analyzed during each run. In all cases, the laboratory was able to calibrate the instruments according to the known values of isotope ratios in the standards.

The UCD stable isotope laboratory completed 18 duplicate measurements of $\delta^{18}O$ and 16 duplicate measurements of δD while the environmental samples from this study were being analyzed. The average difference between the replicates was 0.03 per mil for $\delta^{18}O$ and 0.4 per mil for δD. Another quality assurance check was made by including 13 samples of DI (deionized) water from the USGS laboratory in Sacramento as blind replicates. The standard deviations for 13 measurements of the DI water were 0.07 per mil for $\delta^{18}O$ and 0.8 per mil for δD. Therefore, overall precision of the stable isotope measurements is considered to be better than 0.10 per mil for $\delta^{18}O$ and better than 1.0 per mil for δD.

Results and Discussion

Mercury Concentrations and Loads

Loads were determined using two approaches: (1) during the rainy season, samples were collected during or after storms because of the higher river flows and the greater potential for transport of mercury and methylmercury, and (2) during the dry season samples were collected at planned intervals. The rainy season in northern California is generally between November and March, with little or no rainfall during the remainder of the year. Two representative hydrographs are shown (fig. 2) for representative sites on a tributary (Bear Creek above Holsten Chimney Canyon) and on Cache Creek. At both sites, the peak flows occurred during the rainy season, and extremely low flows occurred during the spring-to-fall dry season. As noted earlier, flows on the main stem of Cache Creek during the dry season are largely controlled through releases of water from Clear Lake or Indian Valley Reservoir (fig. 1). These dry-season releases of water irrigate downstream farms or orchards. Because water is released according to accurate assessment of irrigation needs, the dry season flows of the Cache Creek at Yolo site (fig. 1) are very low, as water is diverted to farms. The Yolo Bypass is used as a flood control channel, and as a result, very little water is present in the Bypass during the dry season. Rainfall was below normal during this study and discharge from Cache Creek was relatively low compared with other years having historical records. The discharge for water year 2000 (October 1, 1999, through September 30, 2000) for Cache

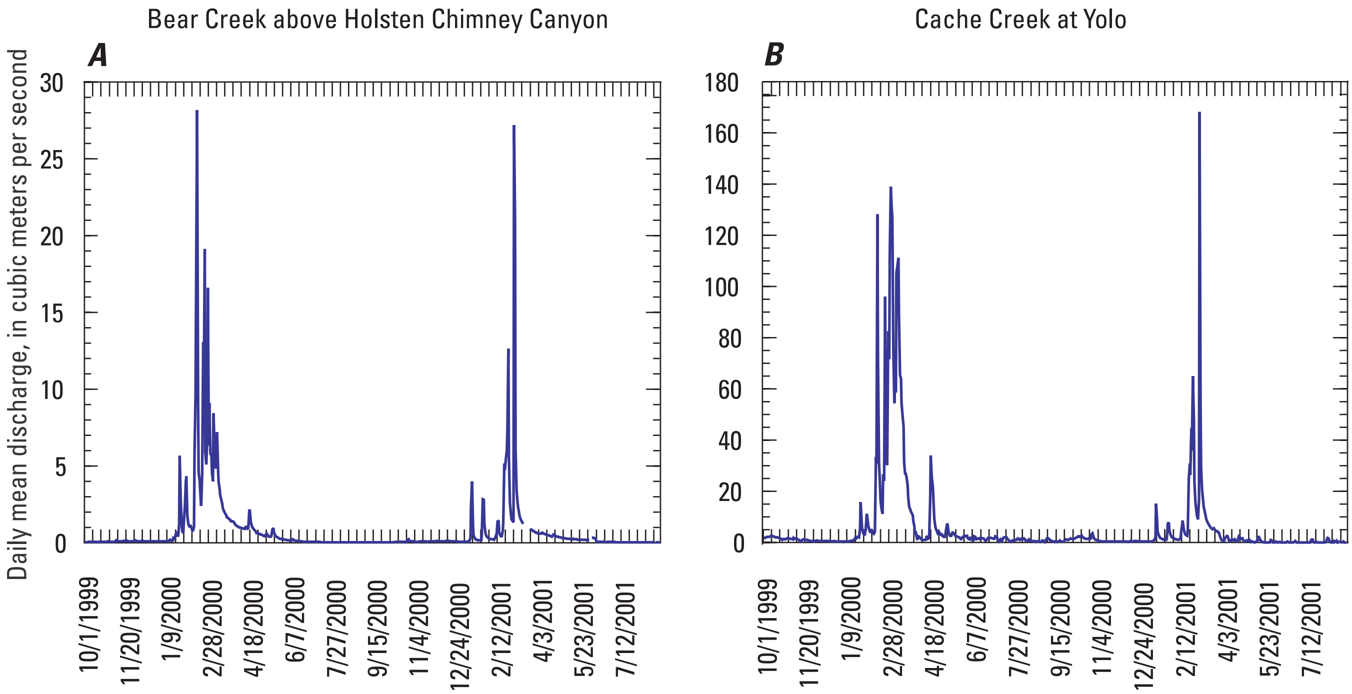

Figure 2. Daily mean discharge for Bear Creek above Holsten Chimney Canyon and Cache Creek at Yolo, Cache Creek Basin, California.

Creek at Yolo was only 55 percent of the average annual discharge for 1903–2000 (Anderson and others, 2001). The previous water year (1999) had higher rainfall, and the annual runoff was more than twice the runoff during water year 2000. Discharge during water year 2001 was even less than that during water year 2000. Therefore, the results of this study reflect low-flow conditions in the Cache Creek drainage basin.

Concentrations of mercury in unfiltered and filtered water samples are shown in figure 3 for the large river sites and in figure 4 for the small stream sites; data are given in table 1 in ppendix 1. As expected, the small stream sites (the mining and geothermal sites—Bear Creek above Holsten Chimney anyon, Sulphur Creek at Wilbur Springs, and Harley Gulch near Wilbur Springs) (figs. 1, 4) had the highest concentrations, and most of the mercury was associated with suspended sediment. Much of the mercury in the suspended sediment, especially that near the mine sites, is probably in the form of cinnabar or metacinnabar, which is very insoluble. These three small stream sites had higher proportions of mercury in filtered water than the large river sites. Mercury passing through the 0.45 µm capsule filter may be truly dissolved or present as very fine colloidal particulates. It is likely that dissolved and (or) colloidal mercury enters the streams near the mines or geothermal springs. Concentrations of mercury were lower at most of the downstream sites (large river sites) than at the mining and geothermal sites because of the greater distance of the downstream sites from the mercury sources and because of dilution by the two largest sources of water, Clear Lake and Indian Valley Reservoir. The ratio of mercury in filtered water to that in unfiltered water tended to be lower at the sites farther downstream (fig. 3).

Concentrations of methylmercury in unfiltered and filtered water samples for selected sites are shown in figures 5 and 6. (See also table 2 in Appendix 1.) The highest concentrations were measured in water from Sulphur Creek at Wilbur Springs, Bear Creek above Holsten Chimney Canyon, and Harley Gulch near Wilbur Springs. Concentrations of methylmercury were higher in unfiltered water samples than in filtered samples. The proportion of methylmercury in the filtered water samples relatiave to the unfiltered samples was higher than the corresponding ratio for total mercury. The ratio of methylmercury in filtered water samples to that in unfiltered water samples ranged from approximately 0.1 to 1.0. There was considerable variability in this ratio at all sites.

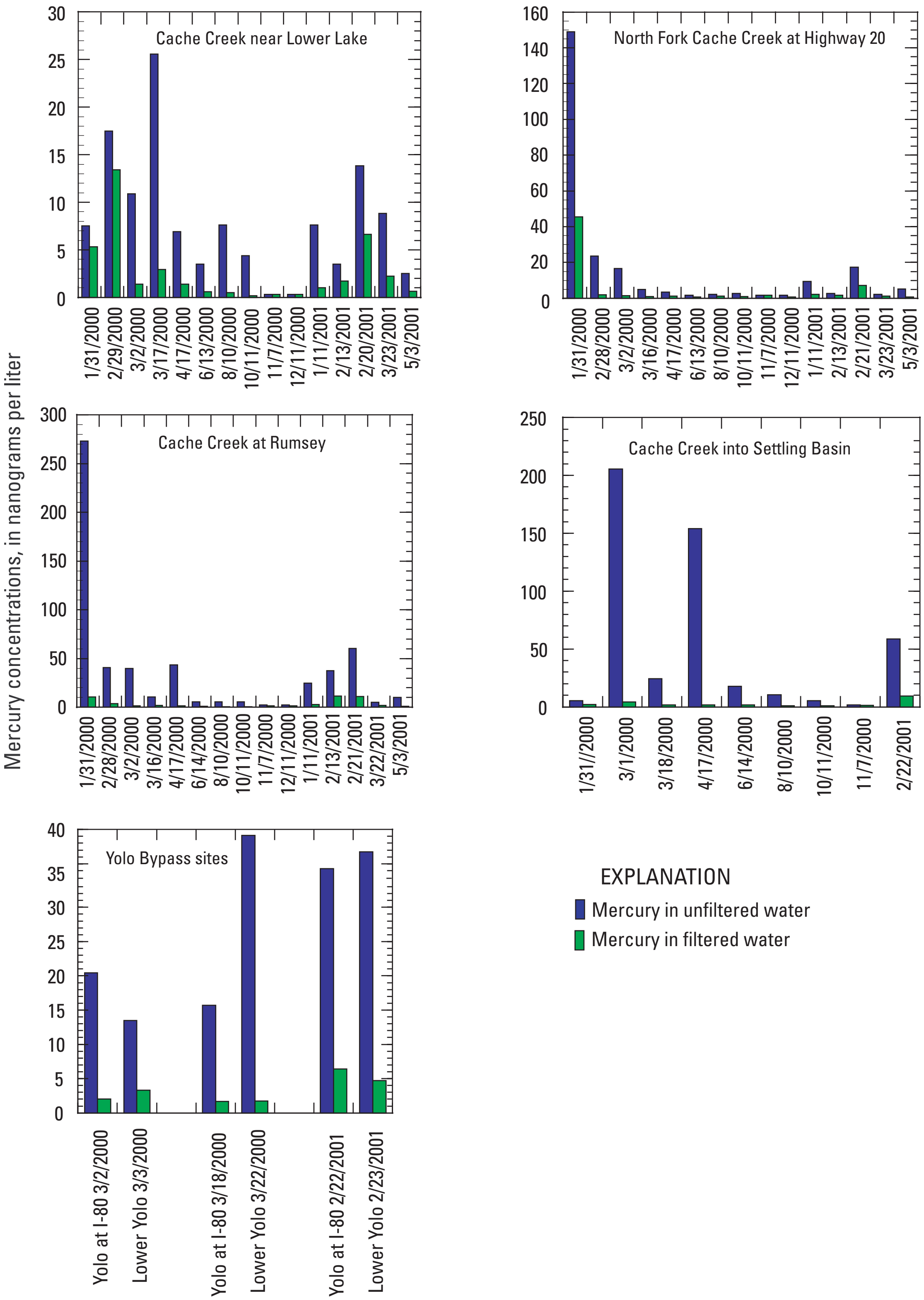

Figure 3. Concentrations of total mercury at large river sites, Cache Creek Basin, California.

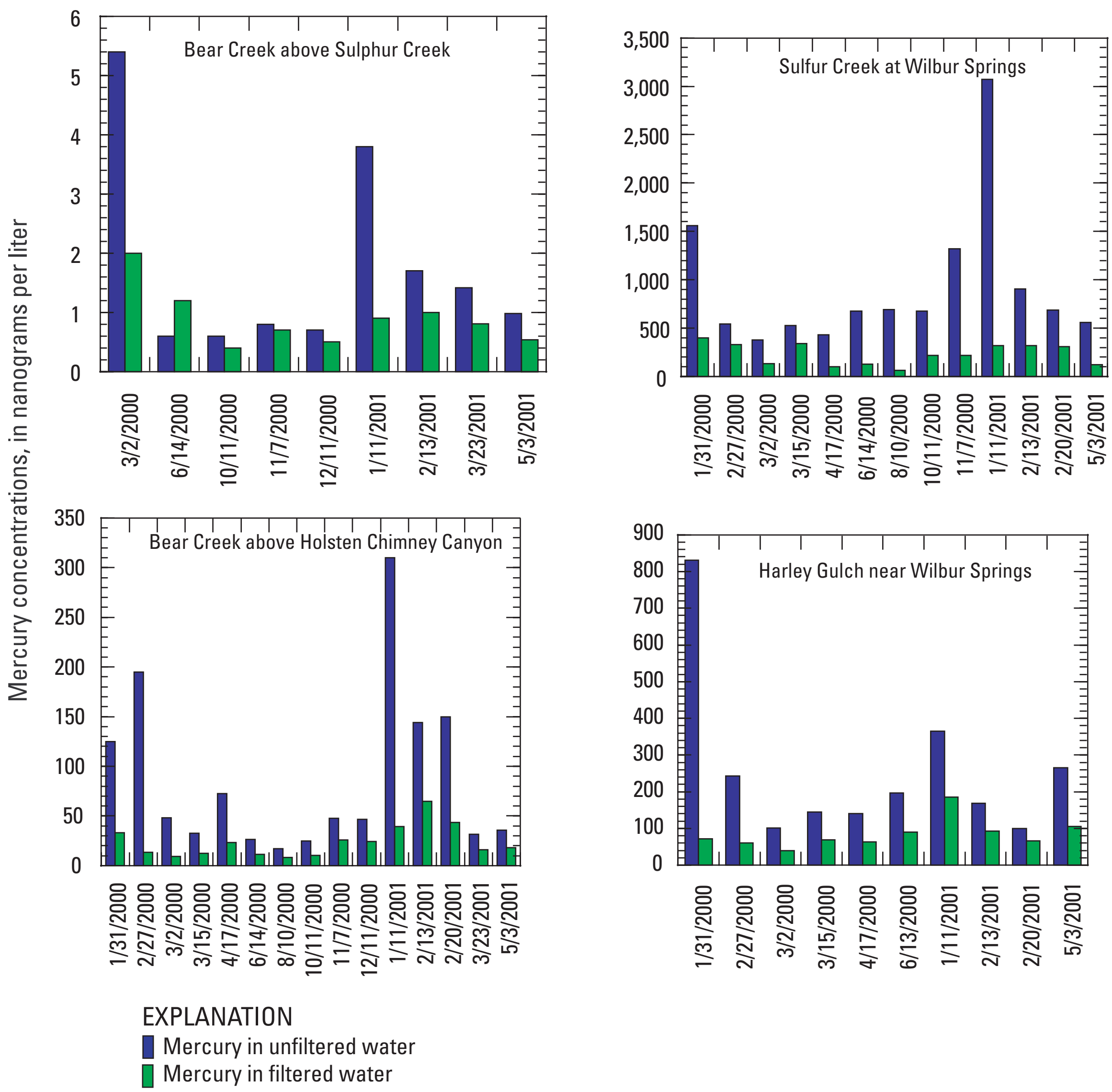

Figure 4. Concentrations of total mercury at small stream sites, Cache Creek Basin, California.

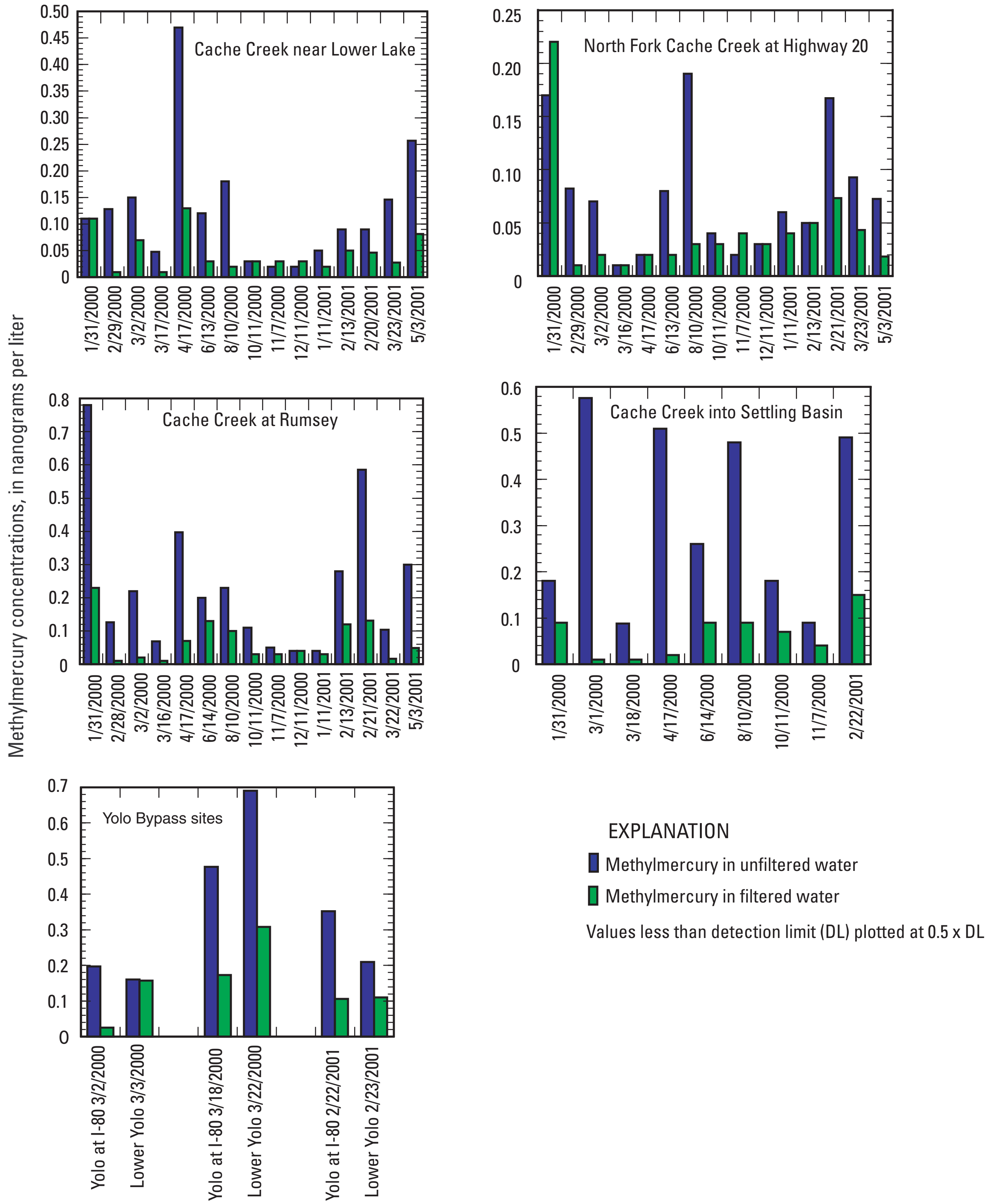

Figure 5. Methylmercury concentrations at large river sites, Cache Creek Basin, California. DL, detection limit.

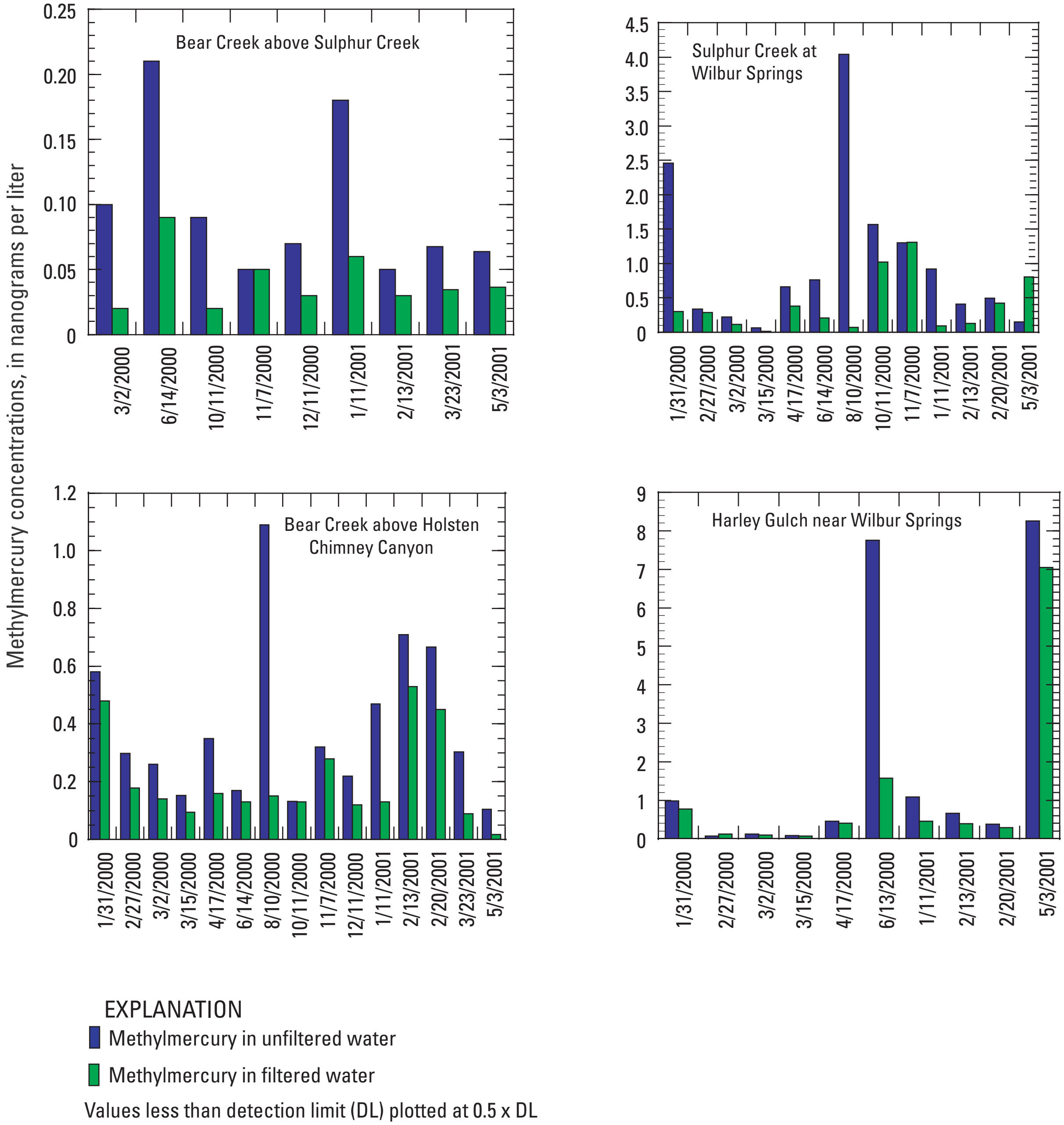

Figure 6. Methylmercury concentrations at small stream sites, Cache Creek Basin, California. DL, detection limit.

Instantaneous loads of total mercury in unfiltered and filtered water for selected sites are shown graphically in figures 7 and 8; instantaneous loads of total mercury are shown on maps in figures 9 (February and March 2000) and 10 (February 2001). The largest loads were measured during the winter rainy season. For the year 2000 sampling (fig. 9), the instantaneous loads of total mercury were low near the mining and geothermal sites (sites 3, 4, and 5 on fig. 1; site names on table 1) relative to the downstream sites because of the lower discharges from the mining and geothermal sites. During the February to March 2000 storm, loads of total mercury increased downstream and exceeded the sum of the loads from the mining and geothermal sites. During February 2000, part of the increase downstream could be attributed to water management or hydrological factors. On February 28, 2000, midway during the period that samples were being collected, water began to be released from the Clear Lake dam to lower water levels of Clear Lake to reduce the risk of flooding. Water is periodically released after winter rains to prevent flooding of homes and businesses near the lakeshore. For example, during sampling, the discharge of Cache Creek at Rumsey and at downstream sites contained both storm-water runoff and water released from Clear Lake, whereas discharge during sampling at the mining and geothermal sites, as well as the sites on the North Fork Cache Creek, contained only storm-water runoff. Therefore, the higher loads at Cache Creek at Rumsey and downstream at Cache Creek into Settling Basin can be logically attributed primarily to higher flows of the released water re-suspending mercury previously deposited in the bottom sediments. Releasing water from Indian Valley Reservoir would have the same effect. The load of total mercury at the sites farthest downstream, that is, the Yolo Bypass at Interstate 80 near West Sacramento and the Lower Yolo Bypass, resulted from combined flows from Cache Creek and the Sacramento River. No attempt was made, nor are data available, to discriminate between these sources.

The mercury loads during the storm in late February 2001 (fig. 10) were much less than those during the storm in February to March 2000 (fig. 9). (Note the difference in scale of the bars on those two figures.) As measured after the storm in February 2001, the sum of the loads originating from a mining and geothermal site (site 3 on fig. 1) approximated the sum of the loads measured at Cache Creek at Rumsey (site 9) and farther downstream. During that storm, there was very low discharge of water from both Clear Lake and Indian Valley Reservoir. As a result, the mercury loads measured downstream at Cache Creek originated mainly from the mining and geothermal sites.

It was not possible to calculate accurate annual loads of mercury or water flux from all the sampling sites, or at all times at individual sites. Continuous records of discharge are available for a limited number of sampling sites. At some sites, instantaneous discharge was measured at the time of sampling and used to calculate instantaneous loads only. Discharge for the input to the Cache Creek Settling Basin can be estimated from the discharge record of the nearby gaging station Cache Creek at Yolo (fig. 1). Although continuous discharge of Cache Creek at Rumsey was recorded, the quality of hydrologic data from that site was considered inadequate for this study to calculate reliable estimates of either chemical loads or water flux. Continuous discharge records are available for Sulphur Creek at Wilbur Springs, Bear Creek above Holsten Chimney Canyon, Harley Gulch near Wilbur Springs, outflow from Clear Lake (Cache Creek near Lower Lake), the upper Yolo Bypass sites, and outflow from Indian Valley Reservoir (North Fork Cache Creek near Clearlake Oaks).

The calculation of the water flux for the Sulphur Creek site shows that discharge from that location (2,784,928 m^3 in water year 2000 and 1,834,695 m^3 in water year 2001) accounted for approximately 1 percent of the discharge of Cache Creek at Yolo in water year 2000 and approximately 2 percent of the discharge in water year 2001. It accounted for approximately 0.1 percent of the discharge of the Yolo Bypass in water year 2000 and just less than 1 percent in water year 2001.

Bear Creek discharged 33,270,771 m^3 in water year 2000 and 18,267,003 m^3 in water year 2001, accounting for approximately 12 percent of the annual discharge of the Cache Creek at Yolo site in water year 2000, and 19 percent in water year 2001. The Bear Creek discharge accounted for approximately 1 percent of the discharge of the Yolo Bypass in water year 2000 and approximately 9 percent in water year 2001.

The discharge of Harley Gulch (395,288 m^3 for water year 2000 and 5,016 m^3 for water year 2001) was less than that of Sulphur Creek or Bear Creek. The discharge of Harley Gulch accounted for approximately 0.15 percent of the discharge of Cache Creek at Yolo during water year 2000 and only 0.005 percent during water year 2001. The discharge of Harley Gulch accounted for approximately 0.01 percent of the discharge of the Yolo Bypass for water year 2000, and an insignificant amount for water year 2001.

The discharge of Cache Creek into the Yolo Bypass (268,342,149 m^3 in water year 2000 and 93,931,485 m^3 in water year 2001) accounted for approximately 8 percent of the discharge of the Yolo Bypass during water year 2000, but 45 percent during water year 2001. The discharge of the Yolo Bypass at Interstate 80 site, estimated using the discharge data from the nearby Yolo Bypass at Woodland gaging station, was 3,384,847,180 m^3 in water year 2000 and 208,324,638 m^3 in water year 2001.

Water release from the Clear Lake dam was 283,815,038 m^3 in water year 2000 and 90,868,105 m^3 in water year 2001. Water release from the Indian Valley Reservoir dam was 129,800,393 m^3 in water year 2000 and 160,754,977 m^3 in water year 2001.

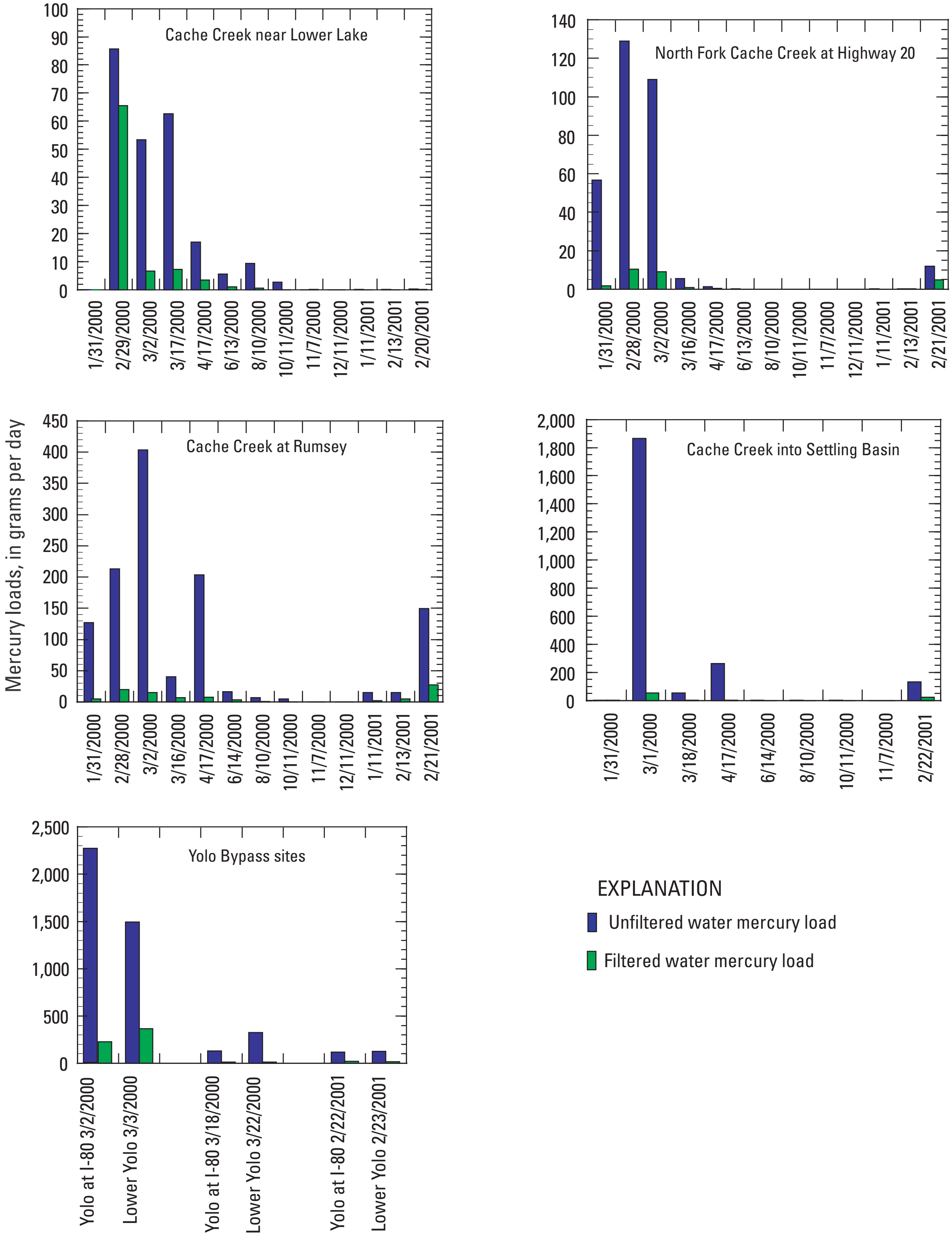

Figure 7. Instantaneous loads of total mercury in unfiltered and filtered water at large river sites, Cache Creek Basin, California.

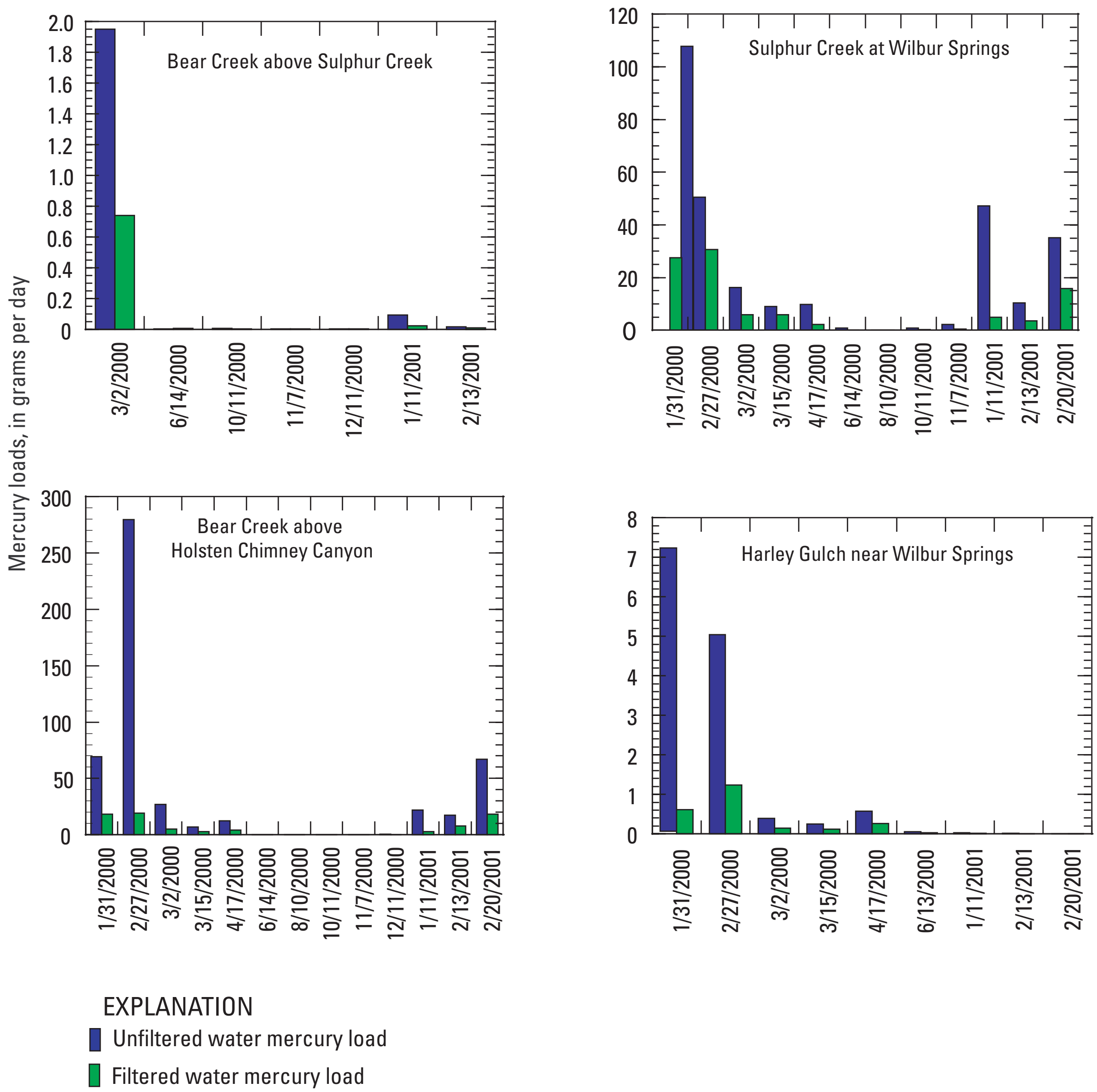

Figure 8. Instantaneous loads of total mercury in unfiltered and filtered water at small stream sites, Cache Creek Basin, California.

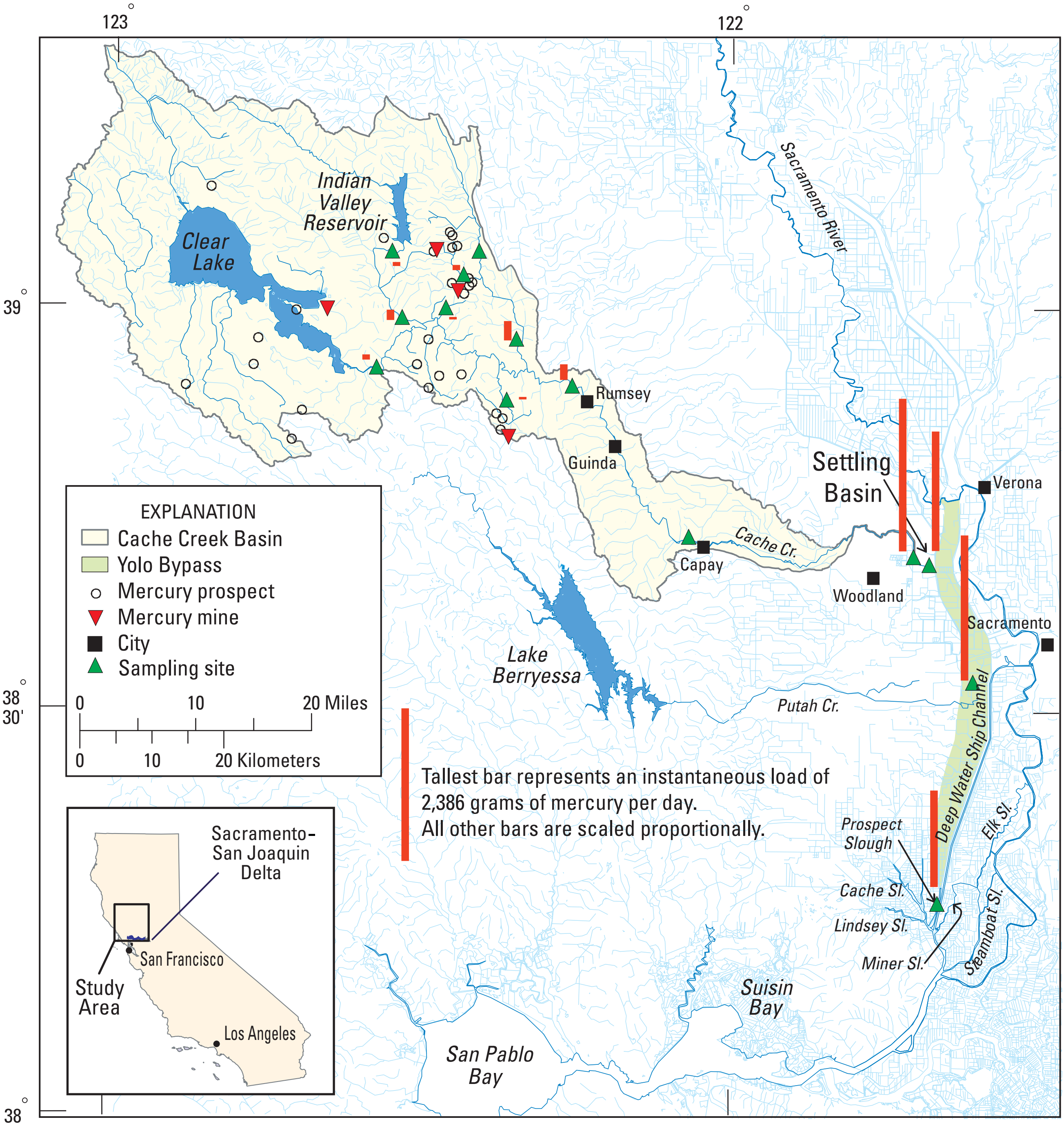

Figure 9. Instantaneous loads of total mercury at selected sites sampled February 27, 2000, through March 3, 2000, Cache Creek Basin, California. Cr., Creek; Sl., slough.

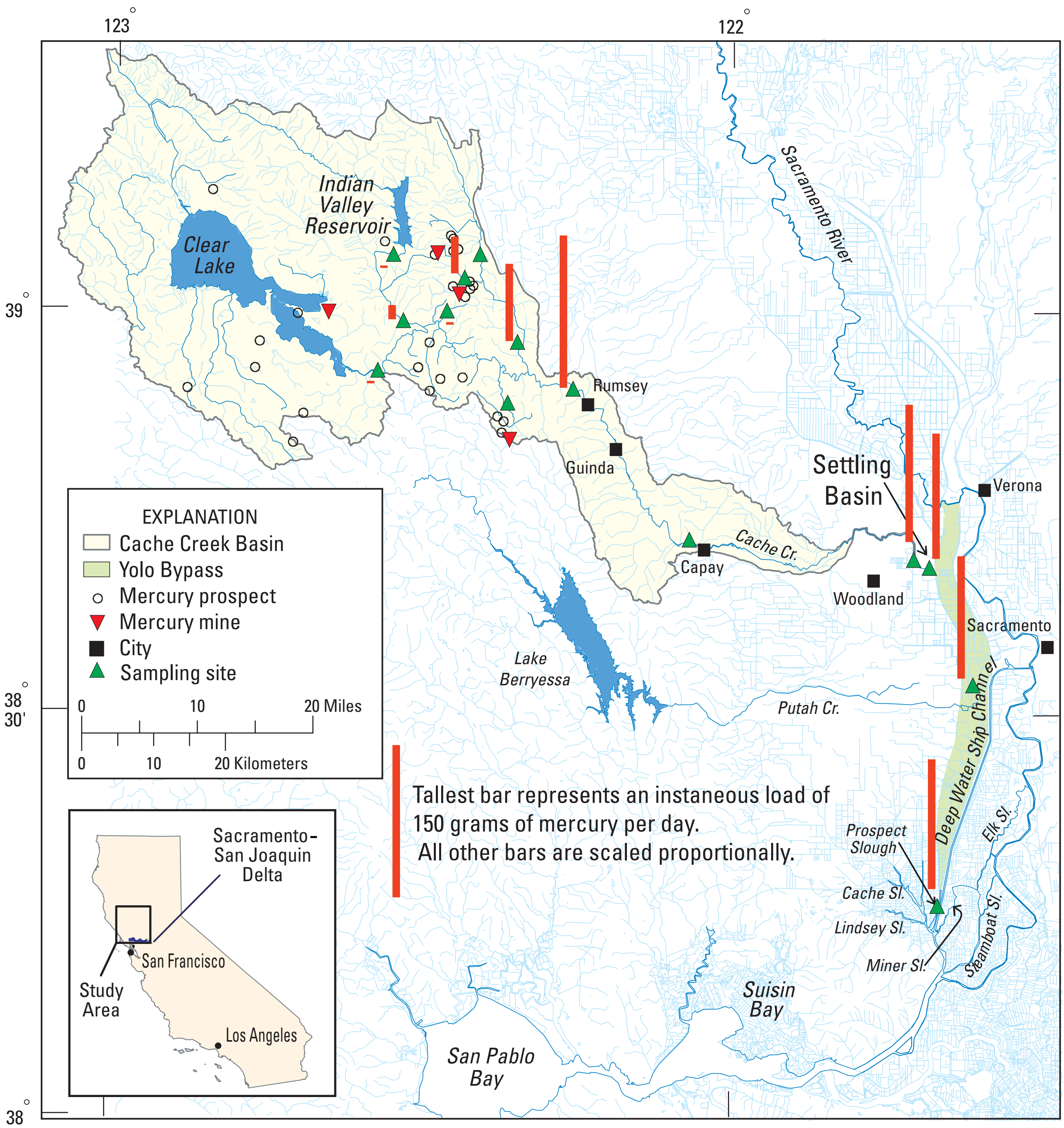

Figure 10. Instantaneous loads of total mercury at selected sites sampled February 20–23, 2001, Cache Creek Basin, California. Cr., Creek; Sl., slough.

A significant relation between stream discharge and the concentration of a constituent is required to calculate an accurate annual load of any constituent in a river for which there is a continuous record of discharge but few measurements of the concentrations of the constituent. Linear least-squares regressions of the data for stream discharge and total mercury concentrations at selected tributary sites and for the input to the Cache Creek into Settling Basin site were low (figure 11). The best relation between stream discharge and mercury concentration was for the Cache Creek into Settling Basin site ($R^2 = 0.7$, where R^2 is the coefficient of determination), but the regression equation had poor predictive value and a positive y-intercept. This lack of a reliable relation between discharge and mercury concentration limited our ability to calculate annual loads of mercury for these streams.

A crude estimate of annual mercury loads at selected sites may be obtained by combining estimated average mercury concentrations for the dry (April through Novemeber) and the wet (December through March) seasons with flow data for sites that have reliable records of discharge. For the Clear Lake outflow, an estimated average of 4 ng/L of mercury for the dry season and an estimated average of 12 ng/L of mercury for the wet-season were used. For the Indian Valley Reservoir, an estimated average of 2 ng/L of mercury for the dry season and 5 ng/L for the wet season were used. For Harley Gulch, an estimated average of 169 ng/L for the dry season and 279 ng/L for the wet season were used. For Bear Creek, concentrations of 38 ng/L and 131 ng/L were used. For Sulphur Creek, values of 758 ng/L and 1,095 ng/L were used. For the Cache Creek Settling Basin, concentrations of 1.3 ng/L and 51.3 ng/L were used.

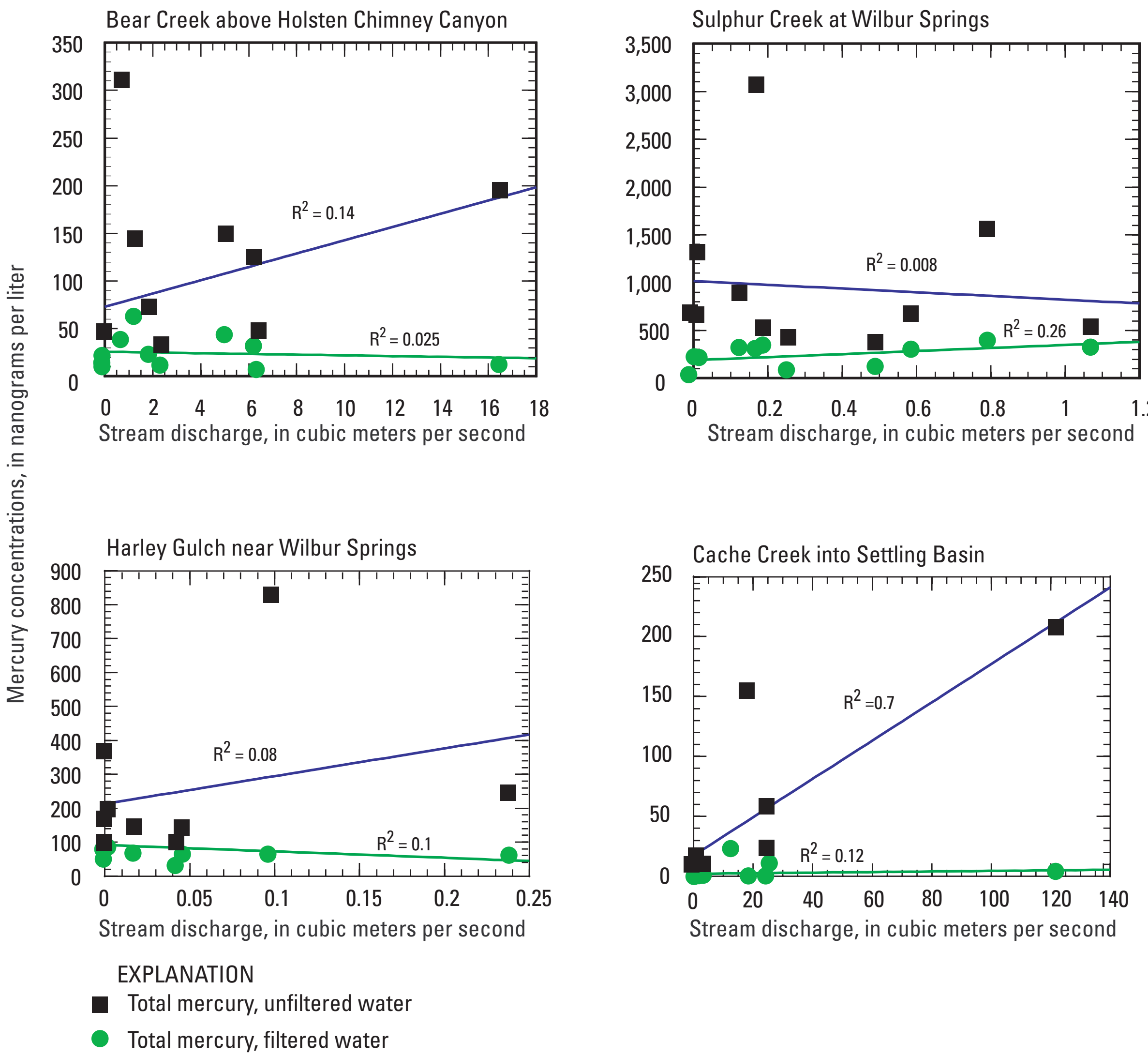

Figure 11. Relation between total mercury concentration and stream discharge at selected sites, Cache Creek Basin, California. R^2 is the coefficient of determination.

The estimated annual loads of mercury in unfiltered water at the Clear Lake outflow were 1,660 g in water year 2000 and 370 g in water year 2001. The estimated annual loads for the outflow from Indian Valley Reservoir were 320 g for both water year 2000 and water year 2001. The estimated annual loads for Bear Creek were 3,670 g for water year 2000 and 1,960 g for water year 2001. The estimated annual loads obtained for Sulphur Creek were 2,850 g for water year 2000 and 1,660 g for water year 2001. The estimated annual load for Harley Gulch was 100 g for water year 2000, but was negligible for water year 2001 because of very low discharge. In both years, the loads from Sulphur Creek, the geothermal source, were greater than those from Harley Gulch, the mining source. The estimated annual loads for the Cache Creek Settling Basin were 12,300 g for water year 2000 and 4,580 g for water year 2001. Annual loads, either estimated or otherwise, for North Fork Cache Creek at Highway 20 and Cache Creek at Rumsey could not be calculated because of incomplete, inaccurate, or poorly documented hydrological records. Estimated annual loads for Yolo Bypass at Interstate 80 near West Sacramento were calculated using the average wet-season value of 23.5 ng/L. The estimated annual loads were 70,370 g in water year 2000 and 4,900 g in water year 2001.

Instantaneous loads of methylmercury in unfiltered and filtered water for selected sites are represented on graphs in figures 12 and 13; instantaneous loads of methylmercury in unfiltered water are represented on maps in figure 14 for February to March 2000 and in figure 15 for February 2001. The upstream loads of unfiltered methylmercury during the February to March 2000 sampling were lower than the downstream loads. During the March 2001 sampling, however, the highest load of total methylmercury was at the Cache Creek at Rumsey site (site 9 on fig. 1); two upstream sites, Bear Creek above Holsten Chimney Canyon (site 3) and the North Fork Cache Creek at Highway 20 (site 7), were apparently the main contributors to this load.

Concentrations (dry weight) of total mercury in streambed sediment collected during the late fall of 2000 are shown on figure 16. As expected, concentrations were considerably higher in the sediments from the mining or geothermal sites (sites 3, 4, and 5 on fig. 1) than in the sediments at the sites downstream on Cache Creek or from the North Fork Cache Creek site. Much of the mercury in the bed sediment downstream of the mines is probably in the form of cinnabar or metacinnabar. Mercury concentrations in sediment have been measured previously in samples from the Cache Creek at Rumsey site and at the Yolo Bypass (Domagalski, 2001). The concentration of mercury in streambed sediment collected from Cache Creek at Rumsey in 1995 was 150 ng/g of dry sediment, whereas the sample collected in 1997 contained 450 ng/g of dry sediment, and the sample collected in 2000 contained 613 ng/g of dry sediment. Streambed sediments at the Yolo Bypass at Interstate 80 site were also sampled in 1997. The concentration of mercury measured in that sample was 310 ng/g of dry sediment, and the sample collected in 2000 contained 288 ng/g of dry sediment.

Mercury mining began more than 150 years ago in the Cache Creek Basin, and abandoned mines continue to contribute waste in the form of mercury-contaminated sediment to locations downstream. It is difficult to estimate the baseline concentration of mercury in streambed sediment had there been no mining. Mercury concentrations were 100 ng/g of dry sediment in streambed sediment collected just below Clear Lake and 87 ng/g of dry sediment in North Fork Cache Creek at Highway 20. These values may approximate the concentrations of mercury in sediment uncontaminated by mining waste; however, the sediments below Clear Lake likely show some influence from historical mining activity at the Sulphur Bank Mine (fig. 1), an Environmental Protection Agency Superfund site located in the Oaks Arm of Clear Lake. Mercury concentrations in sediment from the Cache Creek at Rumsey site are expected to be higher than those upstream at the Clear Lake site (site 1 on fig. 1) because of runoff from geothermal sources and because of naturally occurring mercury in upstream soils. Although no pre-mining background concentration of mercury in sediment could be derived for the Cache Creek at Rumsey site, the present concentrations probably have been influenced by human activities for more than 150 years and almost certainly exceed the pre-mining levels. Because of the anthropogenic influences, the streambed sediments along Cache Creek can be considered as an additional source of mercury to downstream areas.

Chemical Signatures of Water Sources

The water chemistry at different locations within the Cache Creek Basin can vary because of chemical differences between the inflowing waters from different sources. These variations in water chemistry, related to water source, may be useful in determining the sources of mercury or methylmercury at downstream locations if the water associated with each mercury source has a distinguishable geochemical signature. Constituents that may be useful as chemical tracers of sources include the aqueous concentrations of chloride (Cl), sulfate (SO_4), boron (B), lithium (Li), and organic carbon; the amounts of dissolved relative to suspended mercury; and the stable isotopes of hydrogen and oxygen in water.

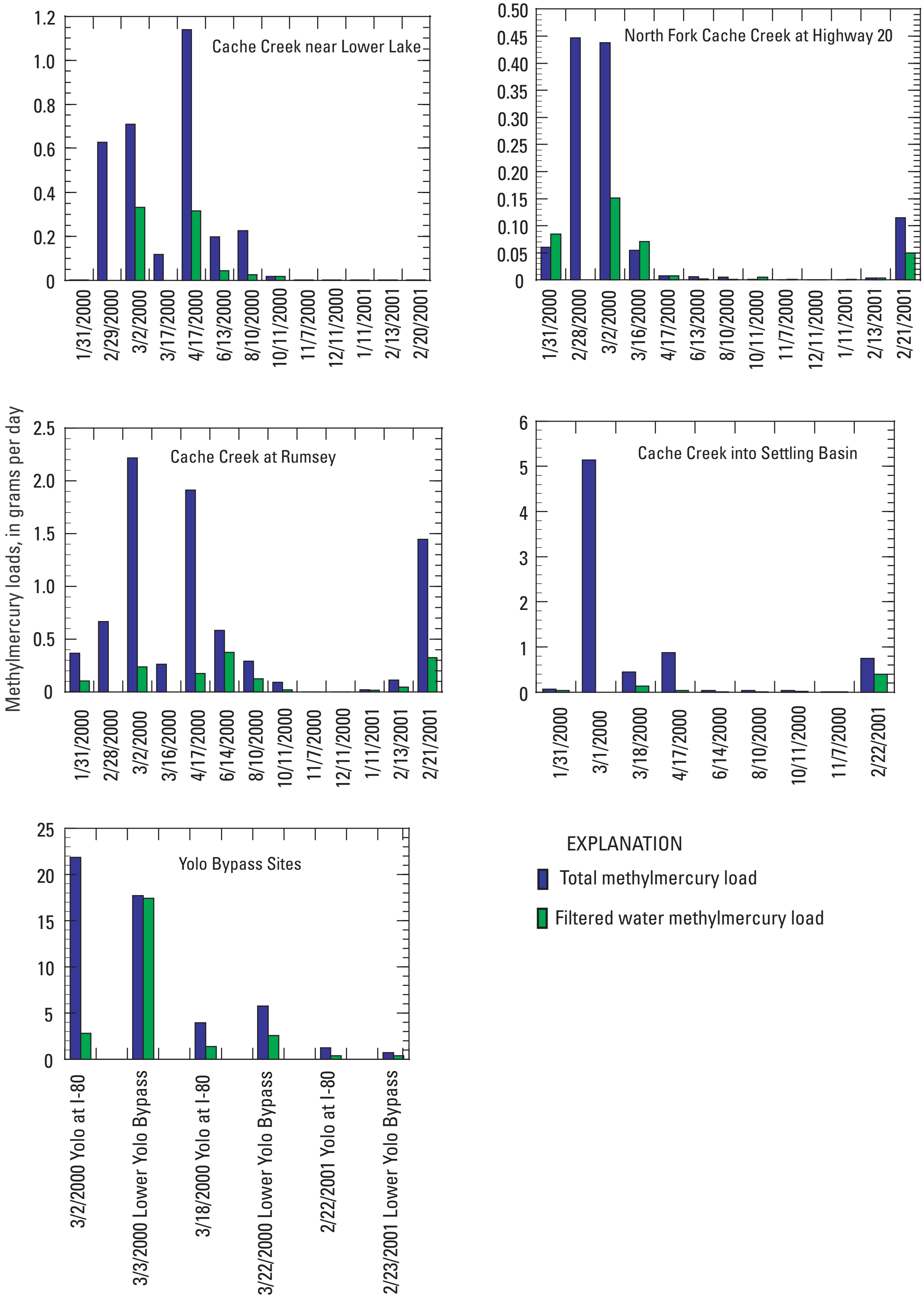

Figure 12. Instantaneous loads of methylmercury in unfiltered and filtered water at large river sites, Cache Creek Basin, California.

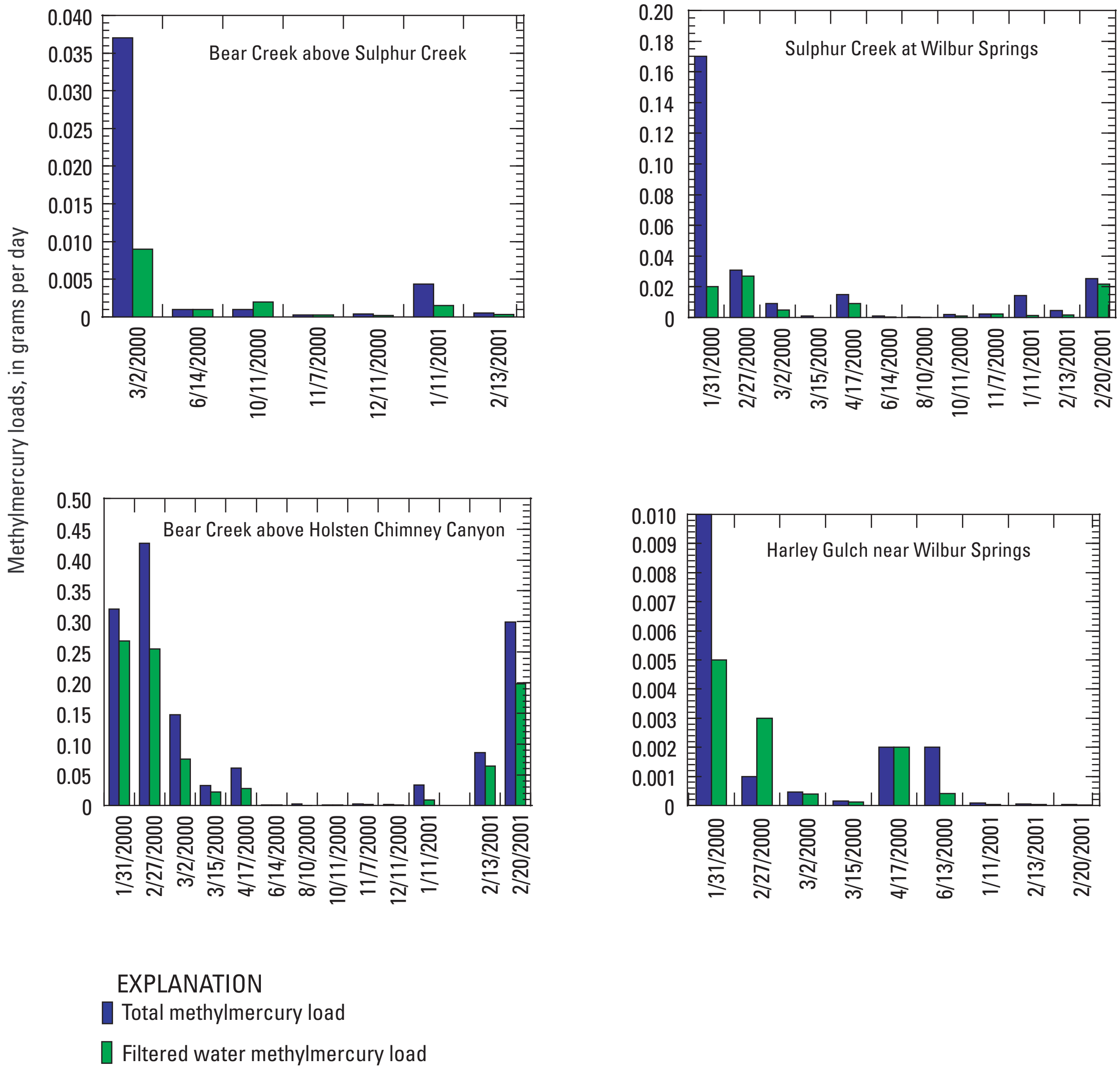

Figure 13. Instantaneous loads of methylmercury in unfiltered and filtered water at small stream sites, Cache Creek Basin, California.

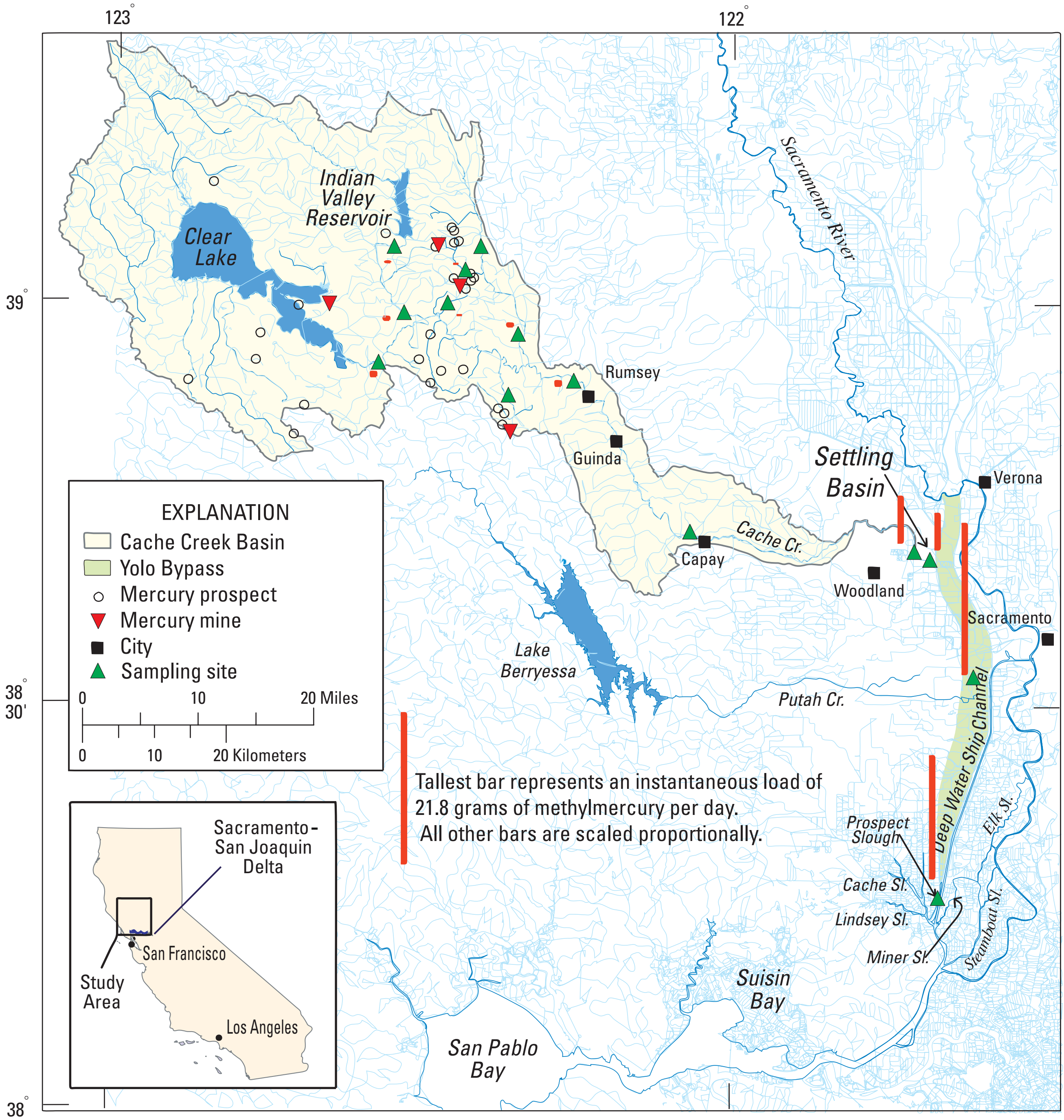

Figure 14. Instantaneous loads of methylmercury at selected sites sampled February 27, 2000, through March 3, 2000, Cache Creek Basin, California. Cr., Creek; Sl., Slough

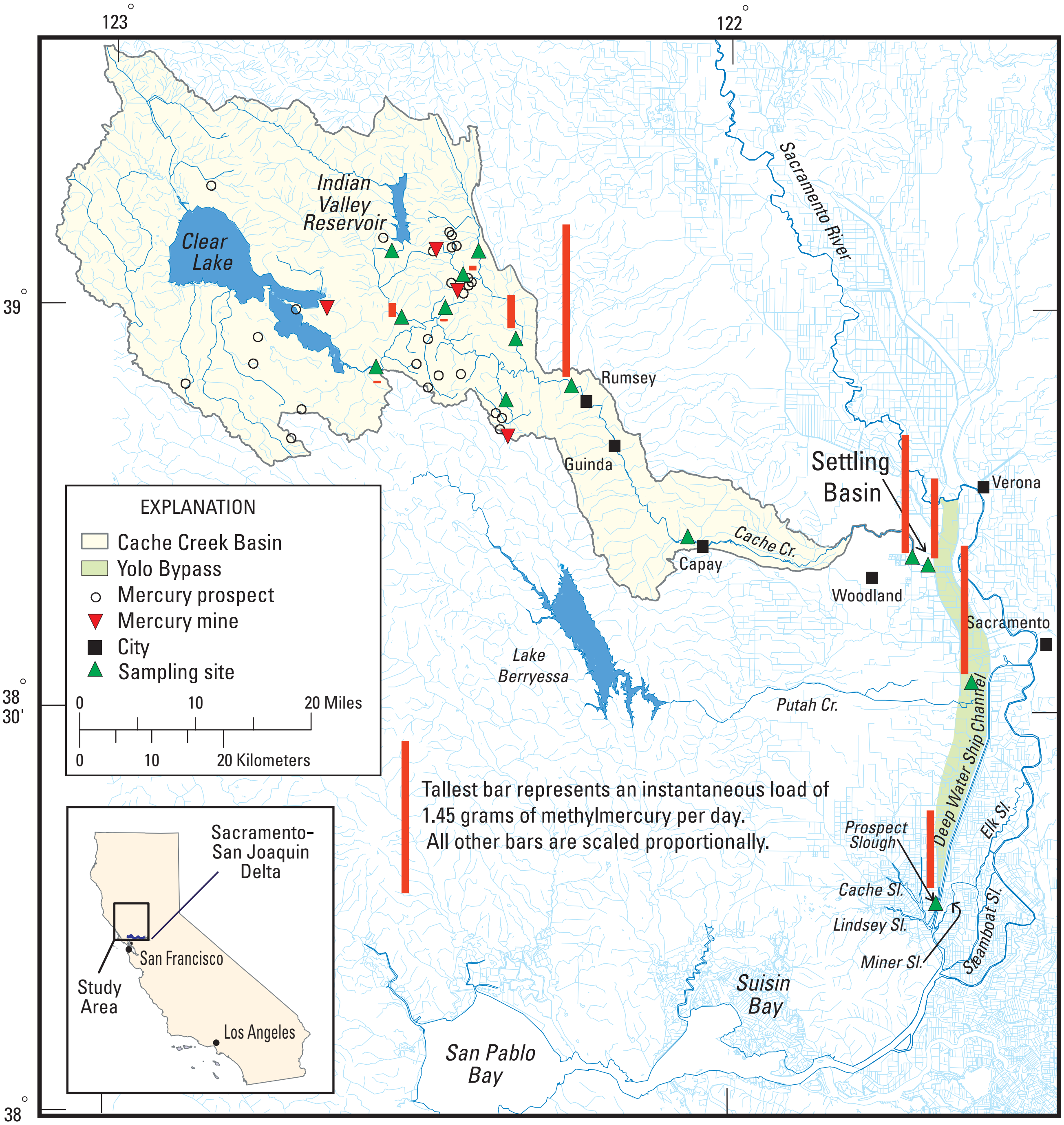

Figure 15. Instantaneous loads of methylmercury at selected sites sampled February 20–23, 2001, Cache Creek Basin, California. Cr., Creek; Sl., Slough

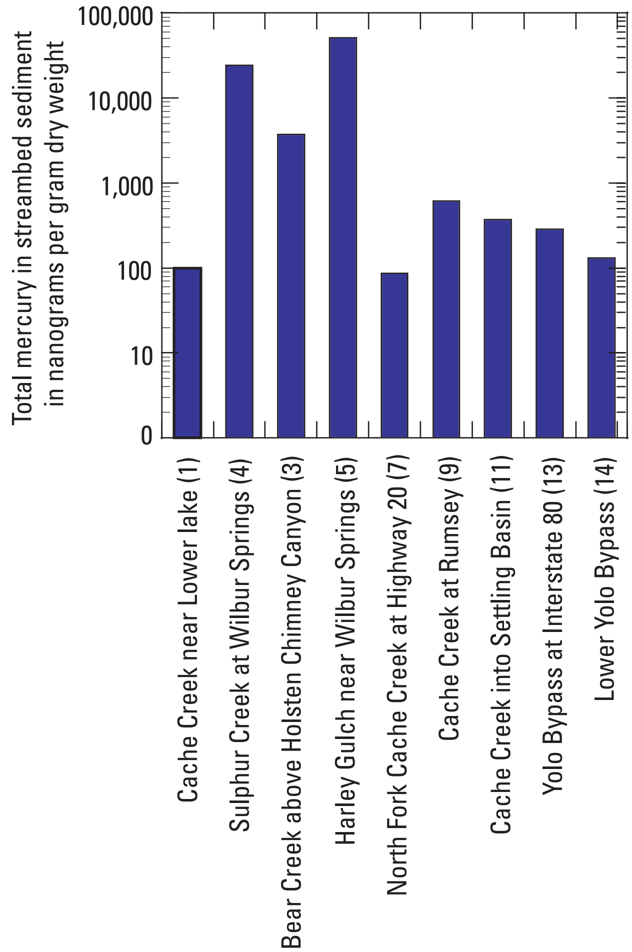

Figure 16. Total mercury in streambed sediment at selected sites sampled during fall of 2000, Cache Creek Basin, California.
Site numbers are in parentheses; locations are on table 1.

Chloride-to-Sulfate Ratios

An example of chemical signatures for the Cache Creek at Rumsey site is the ratio of aqueous chloride to sulfate (Cl/SO_4). A 2-year profile of Cl-to-SO_4 is shown in figure 17 (Domagalski and others, 2000). The Cl-to-SO_4 ratio for Cache Creek water depends on the principal source of water to the creek. The Indian Valley Reservoir has a Cl-to-SO_4 ratio of 3, whereas ratios for Clear Lake are between 1 and 2. Harley Gulch has a relatively low range of Cl-to-SO_4 ratios (0.7–1.25), but Sulphur Creek and Bear Creek have relatively high ratios (28–122 for Sulphur Creek and 14–53 for Bear Creek). The Cl-to-SO_4 ratio for the Cache Creek at Rumsey site depends mostly on whether Clear Lake or the Indian Valley Reservoir is the primary source of water (typically during the irrigation period and wet period), or whether Bear and Sulphur Creeks dominate the flow (typically during the dry period, late fall to early winter). Because of the higher Cl content in the geothermal springs within the Sulphur Creek drainage, the Cl-to-SO_4 ratio increases as the percentage of water from Sulphur Creek increases. The Harley Gulch samples have low Cl-to-SO_4 ratios because of their higher concentrations of sulfate, which is probably derived from the mine waste; retorting (roasting) cinnabar to recover elemental mercury left behind sulfate minerals in the mine waste (Kim and others, 2002), some of which could readily dissolve. The Cl-to-SO_4 ratio for winter storm water runoff indicates a mixed source. The water chemistry, and therefore the Cl-to-SO_4 ratio, changes significantly in the fall. As the irrigation period ends and flows from Clear Lake and Indian Valley Reservoir are decreased, the percentage of water in Cache Creek from Sulphur and Bear Creeks increases. As water containing high concentrations of the Cl ion enter the Bear Creek, the Cl-to-SO_4 ratio increases, and the reduced discharge from either Clear Lake or Indian Valley Reservoir causes the chemistry of Cache Creek to become increasingly similar to that of Sulphur and Bear Creeks.

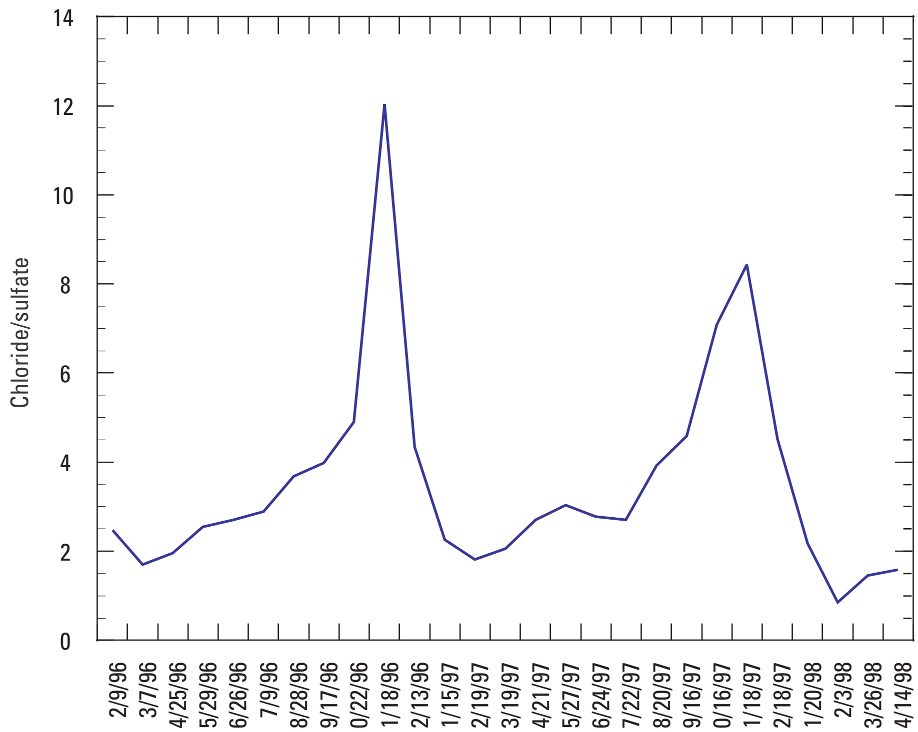

Figure 17. Molar ratio of chloride to sulfate at the Cache Creek at Rumsey site, Cache Creek Basin, California.

Systematic changes in water chemistry throughout the year, as indicated by the changing Cl-to-SO_4 ratio, suggest that differences in other elemental ratios might be useful as tracers to indicate which locations (abandoned mines or geothermal springs) are important sources of mercury or methylmercury to downstream locations. Erosion of geologic material at the mine or geothermal sites, for example, might differ from that of the surrounding geologic material such that runoff from the mine or geothermal sites would have characteristic signatures with respect to element ratios. This is true, as discussed, for Cl/SO_4. To determine if other elements are useful, an analysis of unfiltered water samples was completed by computing the ratios of the amounts of various elements in unfiltered water samples to the amount of aluminum. Aluminum has low solubility, but is a major constituent of the rock types in the Cache Creek Basin. Therefore, normalizing element concentrations in unfiltered water samples to that of aluminum might provide a useful tracer.

Boron-to-Aluminum Ratios

Boron concentrations differed at several locations throughout the Cache Creek Basin. A graph of the ratios of boron to aluminum (B/Al) for mining and other sites within the Cache Creek Basin and at the Yolo Bypass is shown in figure 18. Many of the mining and geothermal sites (such as those of the Abbott and Turkey Run Mines), the Sulphur Creek Mines, sites that are downstream of mines (such as Harley Gulch), and sites downstream of geothermal streams (such as Sulphur Creek at Wilbur Springs) have generally higher B-to-Al ratios than other non-mining or non-geothermal sites. Outflows from the Clear Lake (Cache Creek near Lower Lake) and the upper Bear Creek (Bear Creek above Sulphur Creek) sites have relatively low B-to-Al ratios. The median values of the B-to-Al ratios for outflows from these sites did not differ statistically, according to the Mann-Whitney non-parametric test. The ratios for the upper Bear Creek and the lower Bear Creek (Bear Creek above Holsten Chimney Canyon) sites did differ ($p = 0.0001$, where p is the level of significance) according to the Mann-Whitney non-parametric test. Water from Sulphur Creek probably has the greatest impact on the B-to-Al ratio at the lower Bear Creek site. The B-to-Al ratios for this site and the Sulphur Creek at Wilbur Springs site are similar and are much higher than that for the upper Bear Creek site.

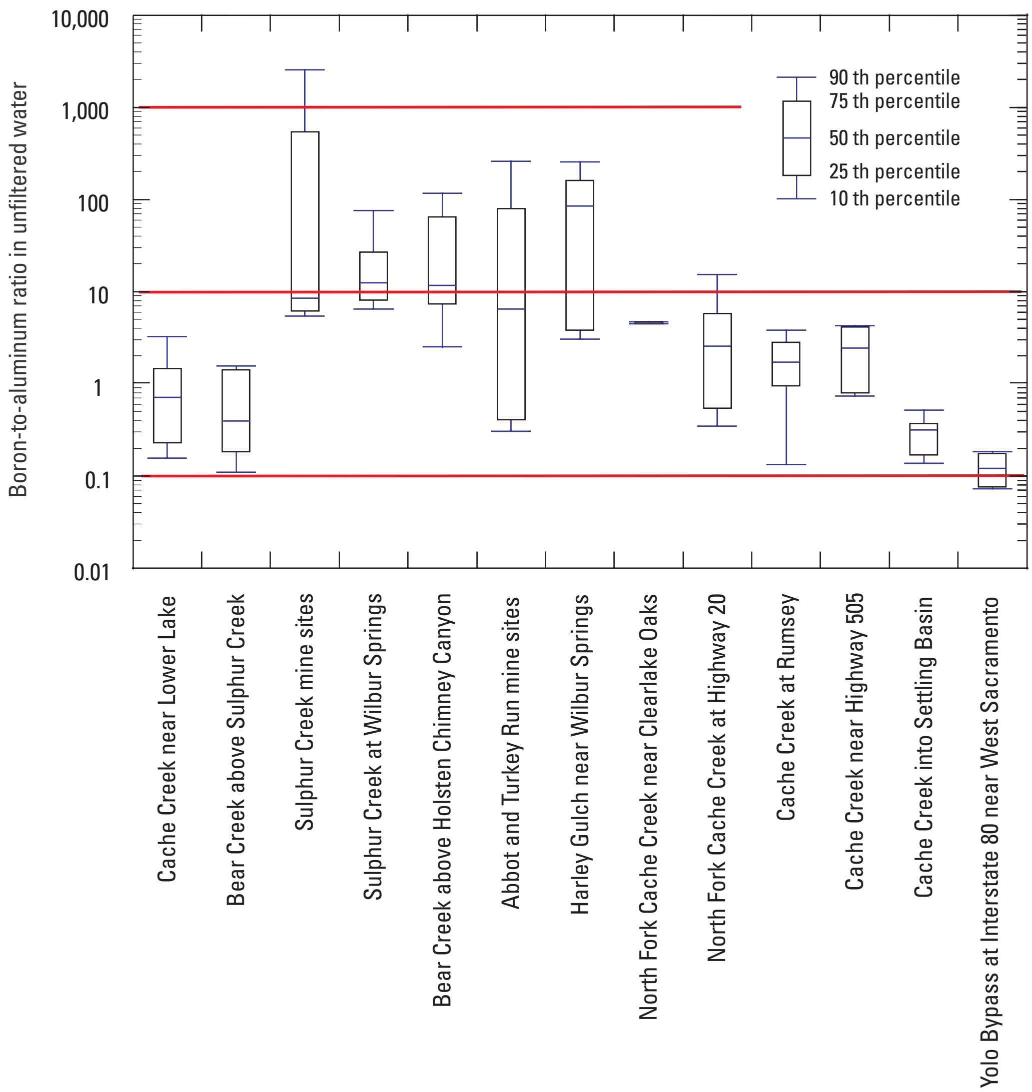

Figure 18. Boron-to-aluminum mass ratios at selected sites of the Cache Creek Basin and Yolo Bypass, California.

The B-to-Al ratios were statistically similar ($p > 0.05$) for Sulphur Creek, the Sulphur Creek mines, the Bear Creek above Holsten Chimney Canyon and the Harley Gulch near Wilbur Springs sites, and the Abbott and Turkey Run mine sites. The B-to-Al ratio for Indian Valley Reservoir outflow (North Fork Cache Creek near Clearlake Oaks) was higher than that for Clear Lake (Cache Creek near Lower Lake), and that influenced the chemistry of the Cache Creek at Rumsey site. The few water samples collected at the outlet of Indian Valley Reservoir (North Fork Cache Creek near Clearlake Oaks) were not sufficient to yield a high confidence level, but those analyzed indicated a higher B-to-Al ratio than that for Clear Lake outflow (Cache Creek near Lower Lake); this higher ratio probably caused an increase in the B-to-Al ratio downstream at the Cache Creek sites near Highway 505 and Rumsey. However, the B-to-Al ratio for the Cache Creek into Settling Basin site, farther downstream, was much lower and similar to that for Clear Lake. Therefore, the mine and geothermal chemical signature of the B-to-Al ratio was distinctive in the upper part of the drainage basin, but was lost before Cache Creek discharged into the Yolo Bypass, at least during the present study.

Boron-to-Lithium Ratios

Although the B-to-Al ratios for water were similar at the geothermal and the mining sites, B and lithium (Li) might co-vary and the concentrations of both B and Li might be highest in geothermal water (Goff and others, 1993a,b). A graph of B and Li concentrations in water from the study sites is shown in figure 19. There is a very good relation between these two elements and the coefficient of determination (R^2) for all sites is 0.987. As expected, the concentrations of B and Li were highest in water from the Sulphur Creek at Wilbur Springs and nearby Sulphur Creek mine sites. There was considerable overlap in ranges of concentrations in water from Sulphur Creek and the Abbott and Turkey Run mine sites and in water from the Harley Gulch site. Because of the discharge of Sulphur Creek into Bear Creek, the B and Li concentrations in the Bear Creek above Holsten Chimney Canyon water samples partially overlapped those of Sulphur Creek and nearby mine sites. The samples from Bear Creek upstream of its confluence with Sulphur Creek (Bear Creek above Sulphur Creek) had the lowest concentrations of B and Li. As was true for the Cl and SO_4 concentrations, the concentrations of B and Li were low in water from Clear Lake and Indian Valley Reservoir, which partially dilutes the concentrations from mine waste or geothermal water in Cache Creek. Concentrations of B and Li at the Cache Creek at Rumsey site were elevated relative to those at the Clear Lake outflow or at North Fork Cache Creek, but it is unclear whether the source of B and Li is the geothermal water or the mine sites.

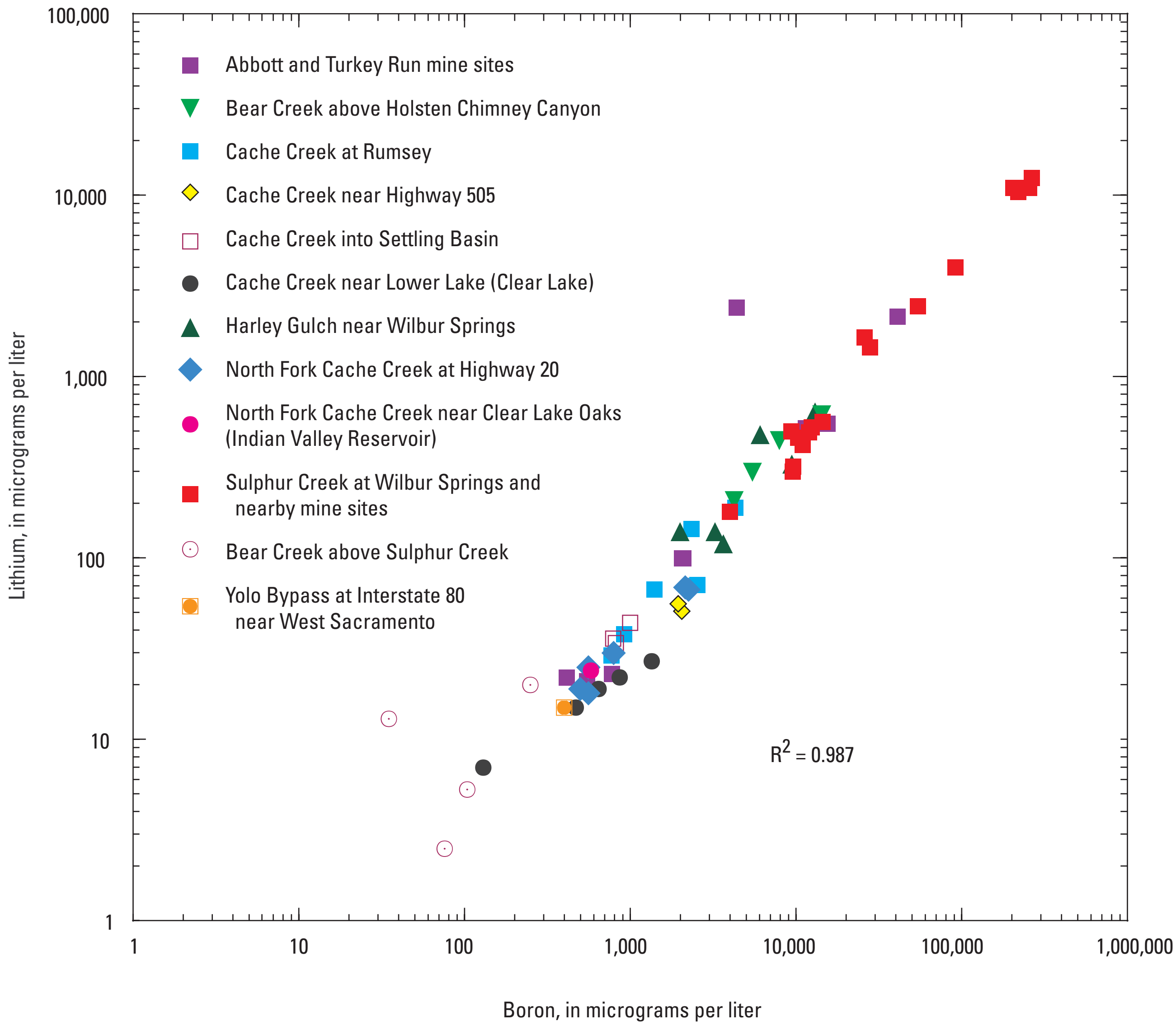

Figure 19. Boron and lithium concentrations at selected sites within the Cache Creek Basin, California. R^2 is the coefficient of determination).

Boron-to-Chloride Ratios

Plots of B and Cl concentrations also indicate the signatures of geothermal waters in the Cache Creek Basin (Donnelly-Nolan and others, 1993; Goff and others, 1993a,b) (fig. 20). As in the case of B and Li, concentrations of B and Cl are strongly correlated; the coefficient of determination (R^2) is 0.98. Measurements of B and Cl concentrations for samples from Sulphur Creek and Sulphur Creek mine sites overlapped those for samples from the Abbott and Turkey Run Mines and Harley Gulch. Cl and B concentrations were highest in samples from Sulphur Creek and the Sulphur Creek Mines. Goff and others (1993b) showed that the high Cl concentrations in Sulphur Creek water can be attributed to relict seawater in the geothermal springs. Figure 20 shows a line of equal B and Cl concentrations. All samples collected during this study plot below this line. Samples from geothermal springs located closer to the Clear Lake volcanic area (Sulphur Bank Mine area, fig. 1) plot on the line of equal B and Cl concentrations (fig. 20), providing a signature different from that for geothermal water from Sulphur Creek (Goff and others, 1993b). The Sulphur Bank geothermal waters differed from those of Sulphur Creek because the waters were near the metamorphic environment near the Clear Lake volcanic area (Goff and others, 1993b). Water having high concentrations of B and Cl in Sulphur Creek mixed with water in Bear Creek resulting in concentrations much higher at Bear Creek above Holsten Chimney Canyon (lower Bear Creek) than at Bear Creek above Sulphur Creek; concentrations at lower Bear Creek overlapped those in Sulphur Creek and at the Sulphur Creek mine sites. Water from locations farther downstream, such as Cache Creek at Rumsey, Cache Creek at Highway 505, and Cache Creek Settling Basin, showed the diluting effect (lower Cl and B concentrations) of Clear Lake outflow and North Fork Cache Creek.

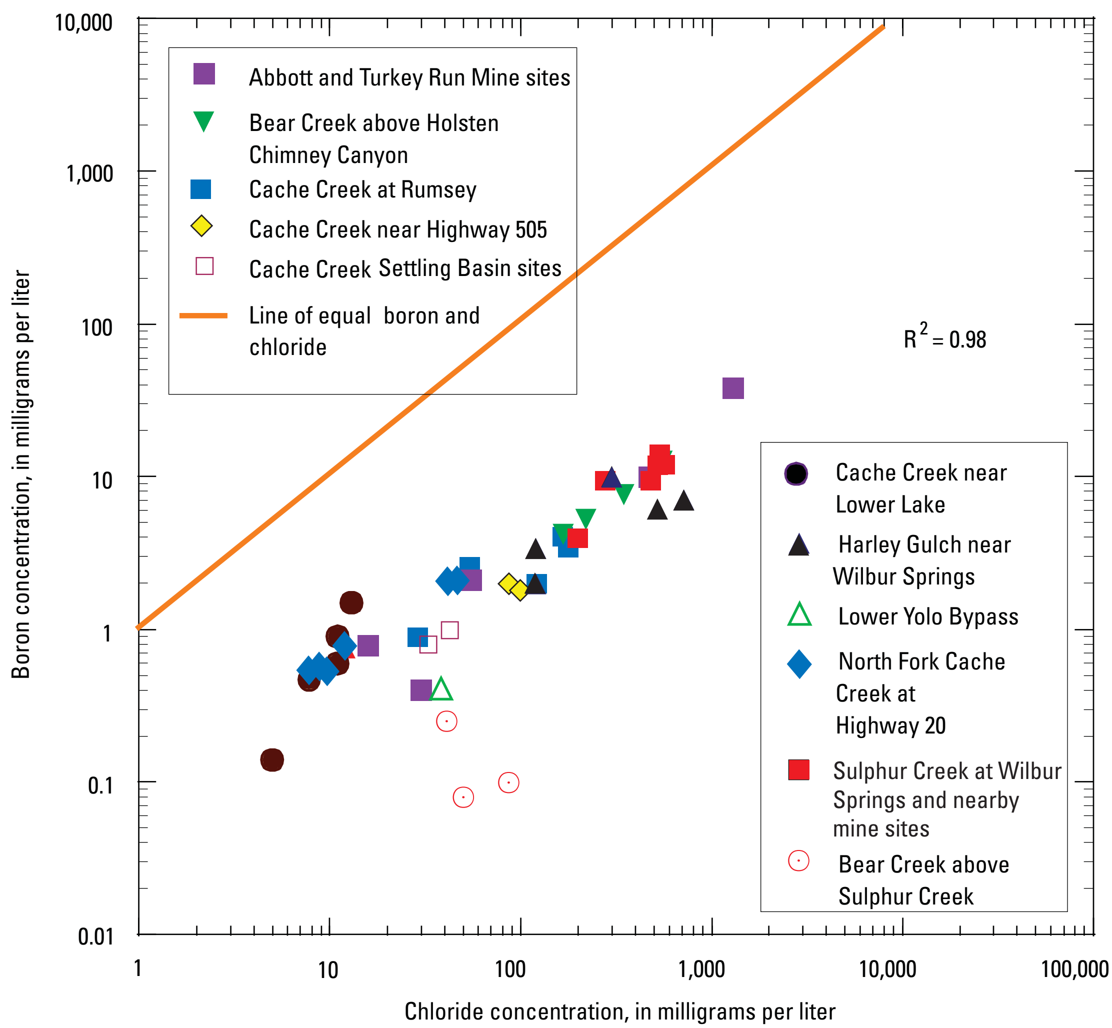

Figure 20. Boron and chloride concentrations at selected sites within the Cache Creek Basin, California. R^2 is the coefficient of determination.

Boron, Chloride, and Sulfate

The molar relation among B, Cl, and SO_4 is shown using a ternary plot (figure 21). A mixing relation of water from Sulphur Creek, the Bear Creek at Holsten Chimney Canyon site, and, in some cases, the Cache Creek at Rumsey and the Cache Creek at Highway 505 sites, is apparent from the plot. The water at Cache Creek at Rumsey has a chemistry similar to that of Sulphur and Bear Creeks in fall when outflows are low after the irrigation season and before the rainfall/runoff season. At other times of the year, the water at Cache Creek at Rumsey is more similar to that of Indian Valley Reservoir or Clear Lake. The water at Cache Creek at Rumsey generally had less boron, or more Cl, than water in Indian Valley Reservoir or Clear Lake. The Abbott and Turkey Run Mines, and Harley Gulch water samples plot along a wide range of Cl and SO_4 levels. It is not possible to distinguish mixing trends of the Abbott and Turkey Run Mines and Harley Gulch waters with downstream sites on Cache Creek using these constituents.

Stable Isotopes of Hydrogen and Oxygen

Another useful signature is the stable isotopic composition of water. Stable isotope data for hydrogen and oxygen in water are given in table 9 of Appendix 1. Hydrogen and oxygen isotope ratios were derived from samples collected from most of the sites of this study (fig. 22). Stable isotope signatures of the geothermal waters also have been previously reported (Goff and others, 1993a,b; 2001). Stable isotope ratios of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ in rain become progressively smaller as air masses leave the ocean and move inland and towards the poles. By definition, ocean water (VSMOW) has values of $\delta^{18}O$ and δD equal to 0.0. Rain and snow (meteoric water) having the smallest values of $\delta^{18}O$ and δD are at the north and south poles (Drever, 1982). Water that plots away from the global meteoric water line usually indicates some type of isotopic fractionation such as may occur during evaporation or certain types of water-rock interactions (Drever, 1982).

Many of the water samples collected during this study had isotopic distributions that plot away from the global meteoric water line (fig. 22), which is based on worldwide stable isotope patterns ($\delta^{18}O$ and δD) in rainfall. In this study, the waters from the Sulphur Creek and the Sulphur Creek mine sites deviated the most from the global meteoric water line. The samples from the Sulphur Creek mine sites had some of the largest values of $\delta^{18}O$, which generated a regression line that deviated the most from the global meteoric water line. The samples from Bear Creek above Holsten Chimney Canyon plotted along an implied mixing line from the Sulphur Creek waters. The large deviation from the global meteoric water line was a unique geochemical signature for the waters of this study. In contrast, the waters from the Abbott and Turkey Run Mines and those from Harley Gulch were more depleted in ^{18}O and plotted closer to the global meteoric water line. The runoff from the Abbott and Turkey Run Mines and the water in Harley Gulch are generally not affected by geothermal discharge and therefore their isotopic distribution is more similar to that of rain.

A second prominent feature of the isotope plot shown in figure 22 is the regression line for the Clear Lake outflow (Cache Creek near Lower Lake). The isotopic signature for that site was similar to those for Cache Creek at Rumsey, Cache Creek at Highway 505, and Cache Creek into Settling Basin. The Clear Lake outflow regression line indicates the isotopic composition of Clear Lake water, which is due to evaporation and local geothermal input over geologic time. The water most depleted in the heavier isotopes is that of the Yolo Bypass. That water plots on or just below the global meteoric water line. Much of the water in the Yolo Bypass originated from the Sacramento River, which is depleted in the heavier isotopes and also plots on the global meteoric water line (Domagalski and others, 2001). Therefore, the isotopic patterns of the geothermal waters are very distinct in the small streams in the upper part of the Cache Creek Basin, but the signature of Clear Lake water dominates at locations on Cache Creek downstream of the mining and geothermal sites.

Plots of chemical constituents and stable isotopes of water molecules can be used to show mixing relations and to evaluate whether or not constituent transport is conservative. Plots of Li versus $\delta^{18}O$ and total mercury versus $\delta^{18}O$ for sites along a flow path from Sulphur Creek to Bear Creek to Cache Creek are shown in figure 23. The water from Sulphur Creek had the highest enrichment in ^{18}O as a the result of a high percentage of geothermal discharge into Sulphur Creek. Elevated concentrations of both Li and mercury in Sulphur Creek water spanned a wide range of oxygen isotope values. The plot for dissolved Li indicates a continuous mixing line from the Sulphur Creek Mines to the Sulphur Creek at Wilbur Springs waters for the samples that are most enriched in ^{18}O ($\delta^{18}O > -2$). In contrast, the plot for mercury does not suggest a continuous mixing line from the Sulphur Creek Mines to Sulphur Creek at Wilbur Springs to Bear Creek above Holsten Chimney Canyon. Dissolved mercury in mine or geothermal waters, originating from locations along Sulphur Creek, probably sorbs to suspended sediment particles and settles to the streambed. Li is probably transported conservatively in these waters because it is dissolved and does not precipitate as a mineral along this flow path or become adsorbed to other sediment particles.

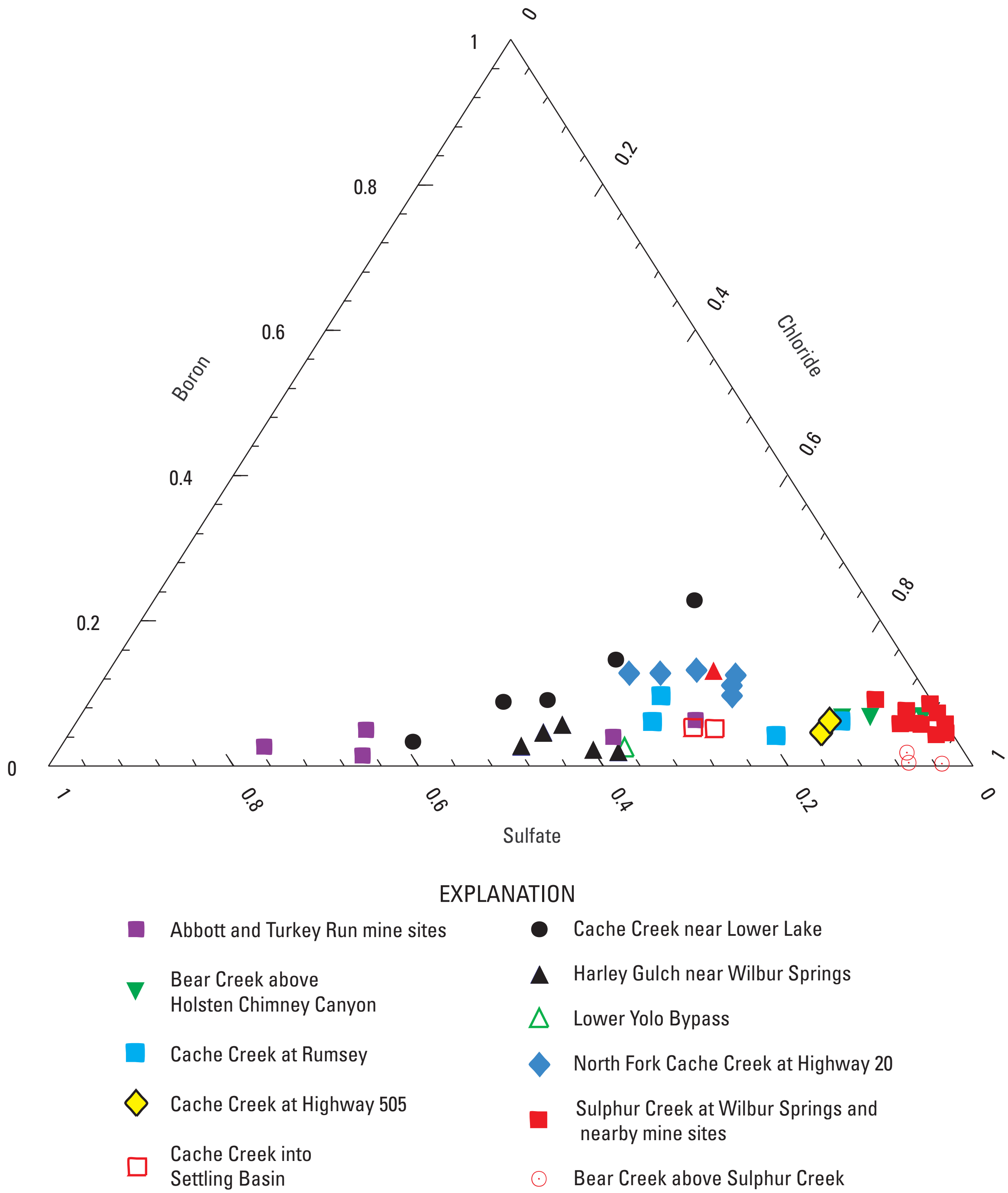

Figure 21. Ternary plot of the molar relation between boron, chloride, and sulfate for selected sites within the Cache Creek Basin, California.

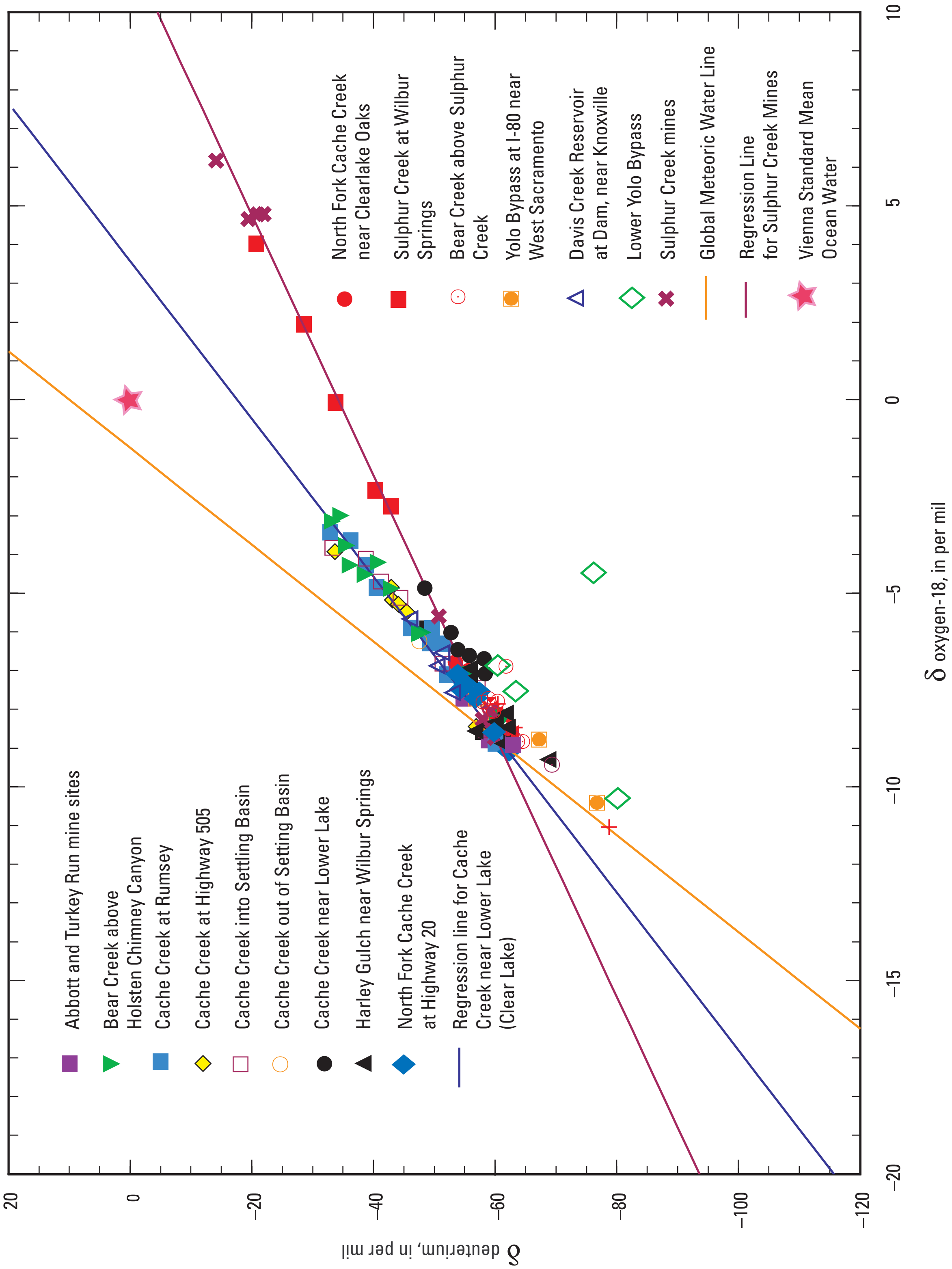

Figure 22. Ratios of stable isotopes (delta [δ] deuterium and δ oxygen-18) for selected sites within the Cache Creek Basin, California.

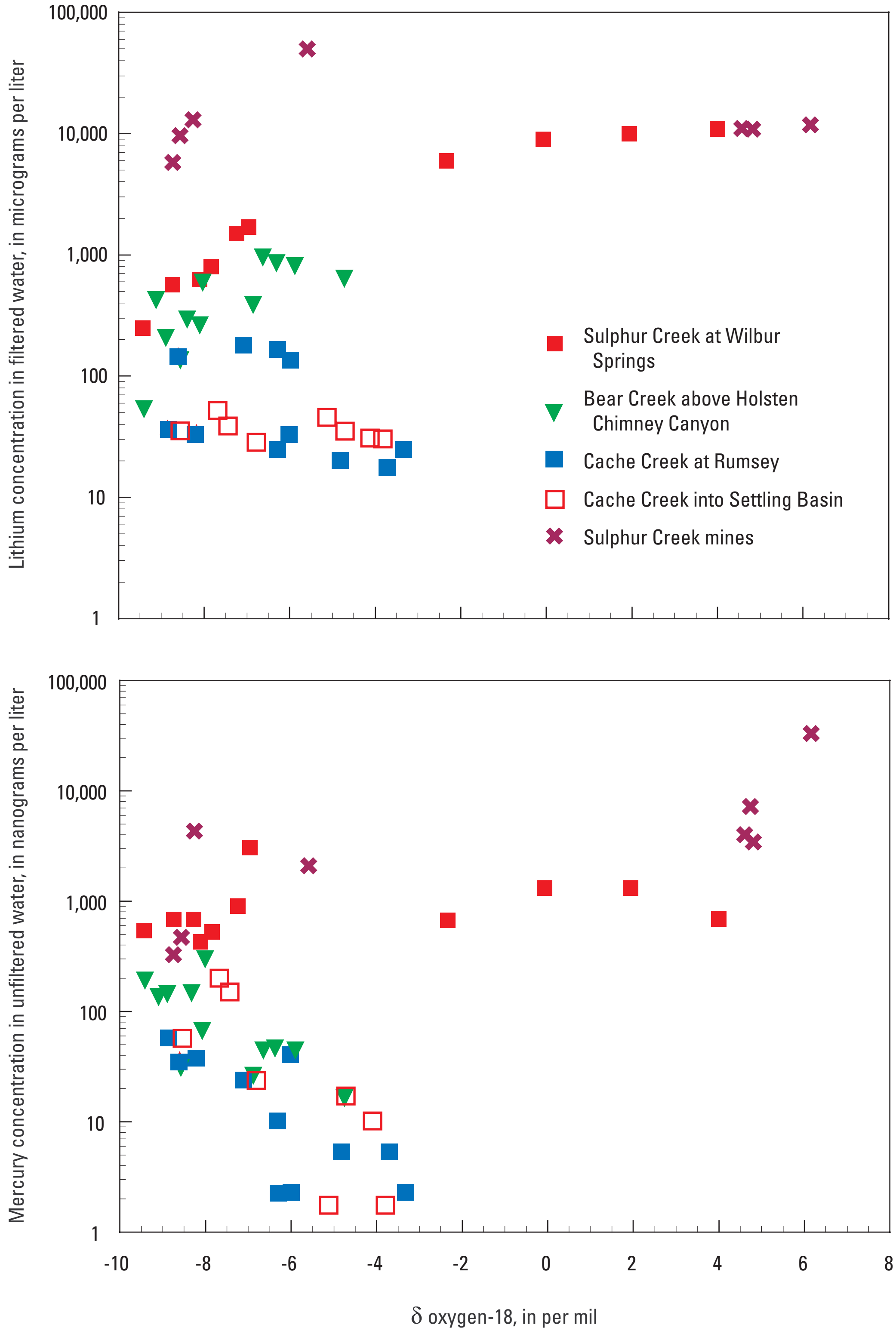

Figure 23. Lithium in filtered water and and mercury in unfiltered water versus delta [δ] oxygen-18 for selected sites within the Cache Creek Basin, California.

Dissolved Organic Carbon

Another chemical relation to consider is that between DOC (dissolved organic carbon) and methylmercury. The Cache Creek at Rumsey site has higher levels of DOC than many other stream sites within the Sacramento River Basin (Domagalski and Dileanis, 2000). Some of the higher levels of DOC can be attributed to outflow from Clear Lake, which is eutrophic. A graph of concentrations of methylmercury and DOC is shown in figure 24. Although higher levels of methylmercury generally correspond to higher levels of DOC, the relation is weak ($R^2 = 0.13$) and, therefore, is a poor predictor. Prior studies within the Sacramento River Basin also have shown that methylmercury concentrations are not correlated with DOC (Domagalski, 2001), even though organic carbon is considered an essential ingredient in the microbially mediated methylation of mercury.

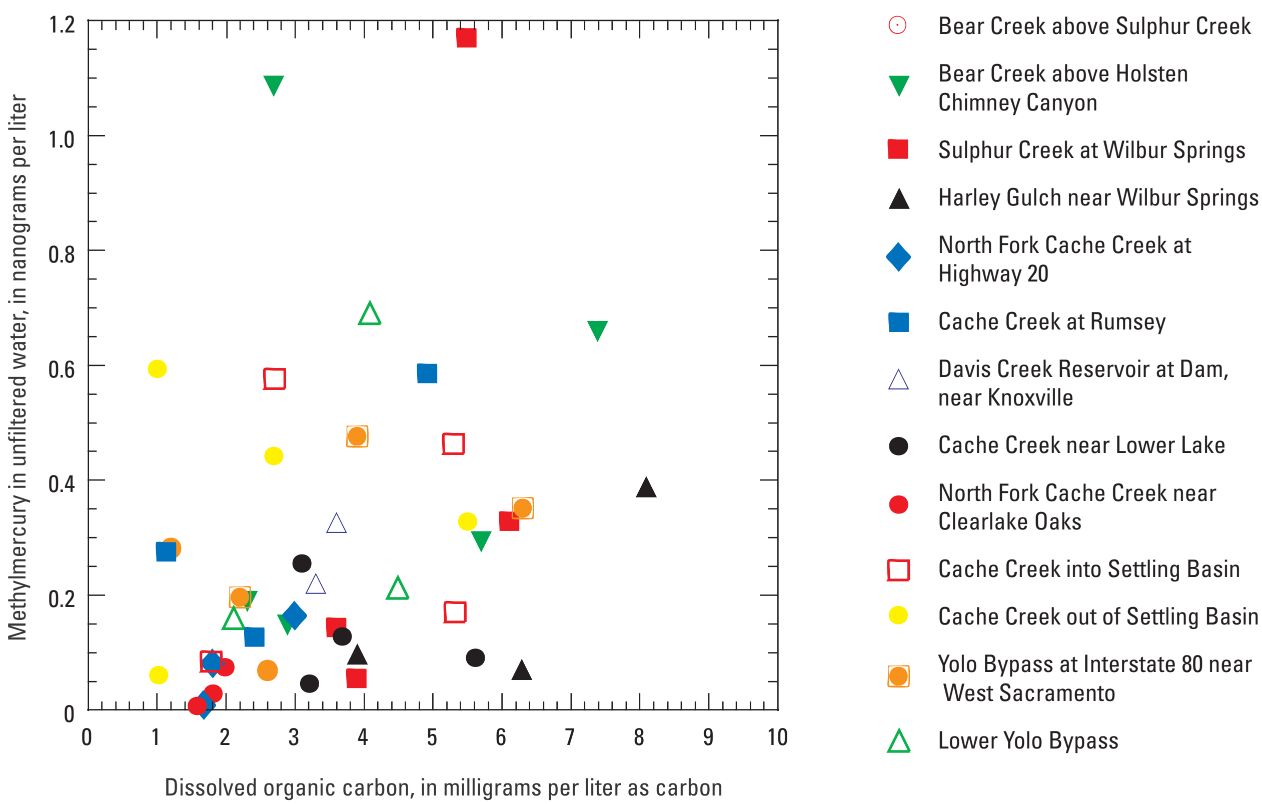

Figure 24. Methylmercury and dissolved organic carbon for selected sites within the Cache Creek Basin, California.

Summary and Conclusions

A 17-month study of mercury and methylmercury concentrations and loads was completed in the Cache Creek drainage basin. Tributaries to Cache Creek located downstream of abandoned mercury mines and near geothermal discharges were sampled for mercury and methylmercury and other aqueous constituents. Other major tributaries to Cache Creek and Cache Creek itself also were sampled at several locations, as was the Yolo Bypass, which receives water from Cache Creek and the Sacramento River during flood conditions. Because of relatively low rainfall during the study period, the stream discharge in this drainage basin was low compared with that noted in historical records. Consequently, observed loads of mercury and methylmercury were probably less than those during years of normal or above-normal precipitation. The largest instantaneous loads of mercury and methylmercury were measured during the winter rainy season. Release of water from either Clear Lake or Indian Valley Reservoir, for the purpose of flood control or to supply irrigation water to downstream farms, also may increase the loads of mercury and methylmercury by re-suspending previously deposited streambed sediment containing elevated concentrations of mercury. Loads of mercury and methylmercury were generally low in the summer months because of low stream discharge. Although the loads of mercury and methylmercury can be low during the dry season, concentrations can be high at any other time of the year.

During the study period, January 2000 through May 2001, loads from geothermal sources of mercury and methylmercury were greater than those from abandoned mining sources. This can be partly attributable to weather patterns that failed to produce large stream flow and erosion from mining waste. Therefore, loads from geothermal sources may not exceed those from abandoned mines during periods of normal or above-normal rainfall. The streambed sediments of the larger streams, such as Cache Creek, also are a significant source of mercury. Re-suspension of Cache Creek streambed sediment and its associated mercury results in the transport of the load downstream. That was especially apparent during the first winter of this study when water was released from Clear Lake to lower the lake level. Therefore, the higher loads at Cache Creek at Rumsey and downstream at Cache Creek into Settling Basin can be logically attributed primarily to higher flows of the released water re-suspending mercury previously deposited in the bottom sediments.

Water from the geothermal and mining locations had different geochemical signatures, especially for stable isotopes of water and other aqueous constituents such as boron, chloride, sulfate, and lithium. The discharges from Clear Lake and Sulphur Creek have distinct stable isotope signatures caused by evaporation and the interaction of water and rock, but these signatures are lost by dilution in lower Cache Creek. The ratio of chloride to sulfate in water samples from Cache Creek at Rumsey shows strong seasonal variations that can be attributed to different sources of water in the drainage basin. The aqueous constituents also are useful as tracers for geothermal sources of water and for evaluating the extent to which mercury is transported conservatively. Concentrations of lithium correlate well with oxygen isotopes along a mixing and dilution flow path from Sulphur Creek to Bear Creek to Cache Creek, indicating that all of these constituents are transported conservatively. In contrast, total mercury in unfiltered water does not correlate well with oxygen isotopes or the other aqueous constituents, indicating that mercury transport is not conservative. It is hypothesized that dissolved mercury from the geothermal sources is largely adsorbed onto fine-grained sediments in Sulphur Creek and lower Bear Creek. Mercury transport in the tributaries dominated by geothermal sources is highly episodic; much of the transport is related to the re-suspension of previously deposited sediment. Mercury transport in tributaries dominated by mining sources such as Harley Gulch is also related to sediment transport mechanisms, as the main form of mercury is hypothesized to be particles of mercury sulfide (cinnabar and metacinnabar).

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Appendix 1. Table 1. Stream discharge and concentrations of mercury in unfiltered and filtered water from sites in the Cache Creek Basin, California

[m^3/s, cubic meter per second; NA, not available; ng/L, nanogram per liter; —, not measured]

Site	Date	Daily mean stream discharge, in m^3/s	Instantaneous stream discharge, in m^3/s	Mercury in unfiltered water, in ng/L	Mercury in filtered water, in ng/L
Bear Creek above Holsten Chimney Canyon	1/31/2000	4.00	—	125	33
Cache Creek at Rumsey	1/31/2000	—	5.40	273	10.6
Cache Creek into Settling Basin	1/31/2000	5.00	—	5.38	2.17
Cache Creek near Lower Lake	1/31/2000	0.15	—	7.48	5.31
Harley Gulch near Wilbur Springs	1/31/2000	0.13	—	831	71.3
North Fork Cache Creek at Highway 20	1/31/2000	—	4.40	149	4.77
Sulphur Creek at Wilbur Springs	1/31/2000	0.62	—	1,560	399
Bear Creek above Holsten Chimney Canyon	2/27/2000	16.60	—	195	13.4
Harley Gulch near Wilbur Springs	2/27/2000	0.21	—	243	60
Sulphur Creek at Wilbur Springs	2/27/2000	1.02	—	542	328
Cache Creek at Rumsey	2/28/2000	—	60.71	40.6	3.75
Davis Creek Reservoir at Dam	2/28/2000	1.90	—	33	6.60
North Fork Cache Creek at Highway 20	2/28/2000	—	63.01	23.7	1.90
Cache Creek near Lower Lake	2/29/2000	51.80	—	17.5	13.40
North Fork Cache Creek near Clearlake Oaks	2/29/2000	65.40	—	5.2	1.85
Cache Creek into Settling Basin	3/1/2000	139.00	—	209	4.10
Cache Creek out of Settling Basin	3/1/2000	139.00	—	161	4.70
Bear Creek above Holsten Chimney Canyon	3/2/2000	5.60	—	48.4	9.13
Bear Creek above Sulphur Creek	3/2/2000	—	4.20	5.38	2.04
Cache Creek at Rumsey	3/2/2000	—	116.70	40	1.48
Cache Creek into Settling Basin	3/2/2000	129.70	—	151	2.11
Cache Creek near Lower Lake	3/2/2000	52.70	—	10.9	1.35
Harley Gulch near Wilbur Springs	3/2/2000	0.04	—	101	39.1
North Fork Cache Creek at Highway 20	3/2/2000	—	75.50	16.7	1.40
Sulphur Creek at Wilbur Springs	3/2/2000	0.42	—	376	135
Yolo Bypass at Interstate 80 near West Sacramento	3/2/2000	1,283.26	—	20.5	2.05
Lower Yolo Bypass	3/3/2000	1,283.26	—	13.5	3.35
Davis Creek Reservoir at Dam	3/10/2000	1.36	—	29.8	5.38
Bear Creek above Holsten Chimney Canyon	3/15/2000	2.60	—	32.7	12.4
Harley Gulch near Wilbur Springs	3/15/2000	0.02	—	144	69.5
Sulphur Creek at Wilbur Springs	3/15/2000	0.18	—	528	342
Cache Creek at Rumsey	3/16/2000	—	43.72	10.6	1.75
Cache Creek at Rumsey	3/16/2000	—	43.20	8.28	1.02
Cache Creek at Highway 505	3/16/2000	—	51.00	16.6	1.05
Davis Creek Reservoir at Dam	3/16/2000	0.54	—	9.65	3.95
North Fork Cache Creek at Highway 20	3/16/2000	—	12.72	5.05	0.85
North Fork Cache Creek at Highway 20	3/16/2000	—	12.70	4.13	0.88
Cache Creek near Lower Lake	3/17/2000	5.90	—	25.6	2.95
North Fork Cache Creek near Clearlake Oaks	3/17/2000	7.70	—	3.5	3.05
Cache Creek into Settling Basin	3/18/2000	26.60	—	24.3	1.50

Appendix 1. Table 1. Stream discharge and concentrations of mercury in unfiltered and filtered water from sites in the Cache Creek Basin, California—*Continued*

Site	Date	Daily mean stream discharge, in m^3/s	Instantaneous stream discharge, in m^3/s	Mercury in unfiltered water, in ng/L	Mercury in filtered water, in ng/L
Cache Creek out of Settling Basin	3/18/2000	26.60	—	11.2	1.60
Yolo Bypass at Interstate 80 near West Sacramento	3/18/2000	96.32	—	15.7	1.65
Lower Yolo Bypass	3/22/2000	96.32	—	39.2	1.75
Bear Creek above Holsten Chimney Canyon	4/17/2000	2.12	—	72.4	23.3
Cache Creek at Rumsey	4/17/2000	—	54.40	43.3	1.62
Cache Creek into Settling Basin	4/17/2000	16.80		154	1.51
Cache Creek at Highway 505	4/17/2000	—	42.50	43.4	1.72
Cache Creek near Lower Lake	4/17/2000	28.30	—	6.91	1.42
Harley Gulch near Wilbur Springs	4/17/2000	0.05	—	140	63.6
North Fork Cache Creek at Highway 20	4/17/2000	—	4.10	3.45	1.21
Sulphur Creek at Wilbur Springs	4/17/2000	0.26	—	430	99.3
Cache Creek near Lower Lake	6/13/2000	19.70	—	3.49	0.63
Davis Creek above Davis Creek Reservoir	6/13/2000	0.01	—	49.9	8.95
Davis Creek below Davis Creek Reservoir	6/13/2000	0.00	—	6.31	4.73
Harley Gulch near Wilbur Springs	6/13/2000	0.00	—	197	89.6
North Fork Cache Creek at Highway 20	6/13/2000		0.85	1.84	0.83
Bear Creek above Holsten Chimney Canyon	6/14/2000	0.09	—	26.5	11.3
Bear Creek above Sulphur Creek	6/14/2000	—	0.07	0.65	1.20
Cache Creek at Rumsey	6/14/2000	—	34.55	5.61	1.17
Cache Creek into Settling Basin	6/14/2000	1.70	—	17.7	1.71
Cache Creek at Highway 505	6/14/2000	—	0.85	11.2	1.62
Sulphur Creek at Wilbur Springs	6/14/2000	0.01	—	676	125
Bear Creek above Holsten Chimney Canyon	8/10/2000	0.04	—	17.3	8.40
Cache Creek at Rumsey	8/10/2000	—	14.70	5.64	0.73
Cache Creek into Settling Basin	8/10/2000	0.88	—	10.6	1.14
Cache Creek at Highway 505	8/10/2000	—	0.30	2.38	1.99
Cache Creek near Lower Lake	8/10/2000	15.60	—	7.57	0.47
Davis Creek above Davis Creek Reservoir	8/10/2000	0.00	—	114	8.26
North Fork Cache Creek at Highway 20	8/10/2000	—	0.30	2.17	1.05
Sulphur Creek at Wilbur Springs	8/10/2000	0.00	—	690	63.3
Bear Creek above Holsten Chimney Canyon	10/11/2000	0.10	—	24.6	10.5
Bear Creek above Sulphur Creek	10/11/2000	0.09	—	0.62	0.39
Cache Creek at Rumsey	10/11/2000	—	9.60	5.67	0.45
Cache Creek into Settling Basin	10/11/2000	2.40	—	5.51	0.85
Cache Creek at Highway 505	10/11/2000	1.00	—	2.19	0.80
Cache Creek near Lower Lake	10/11/2000	7.70	—	4.38	0.24
North Fork Cache Creek at Highway 20	10/11/2000	—	0.20	2.64	0.87
Sulphur Creek at Wilbur Springs	10/11/2000	0.01	—	676	216
Davis Creek above Davis Creek Reservoir	11/6/2000	0.00	—	52.6	7.60
Davis Creek below Davis Creek Reservoir	11/6/2000	—	0.00	5.90	3.50
Bear Creek above Holsten Chimney Canyon	11/7/2000	0.09	—	47.4	25.7

Appendix 1. Table 1. Stream discharge and concentrations of mercury in unfiltered and filtered water from sites in the Cache Creek Basin, California—*Continued*

Site	Date	Daily mean stream discharge, in m^3/s	Instantaneous stream discharge, in m^3/s	Mercury in unfiltered water, in ng/L	Mercury in filtered water, in ng/L
Bear Creek above Sulphur Creek	11/7/2000	—	0.09	0.80	0.70
Cache Creek at Rumsey	11/7/2000	—	0.57	2.40	1.70
Cache Creek into Settling Basin	11/7/2000	0.48		1.80	1.30
Cache Creek at Highway 505	11/7/2000		0.71	1.20	1.10
Cache Creek near Lower Lake	11/7/2000	0.13		0.30	0.30
North Fork Cache Creek at Highway 20	11/7/2000		0.23	1.80	1.60
Sulphur Creek at Wilbur Springs	11/7/2000	0.02	—	1,320	219
Bear Creek above Holsten Chimney Canyon	12/11/2000	0.11	—	46.5	24.5
Bear Creek above Sulphur Creek	12/11/2000	—	0.07	0.70	0.50
Cache Creek at Rumsey	12/11/2000	—	0.85	2.30	1.50
Cache Creek at Highway 505	12/11/2000	—	0.99	1.40	0.80
Cache Creek near Lower Lake	12/11/2000	0.11	—	0.30	0.30
North Fork Cache Creek at Highway 20	12/11/2000		0.28	1.80	0.60
Bear Creek above Holsten Chimney Canyon	1/11/2001	2.40	—	310	39.2
Bear Creek above Sulphur Creek	1/11/2001	—	0.28	3.80	0.90
Cache Creek at Rumsey	1/11/2001	—	7.08	24.9	2.90
Cache Creek at Highway 505	1/11/2001	—	1.93	5.20	1.20
Cache Creek near Lower Lake	1/11/2001	0.14	—	7.60	1.00
Harley Gulch near Wilbur Springs	1/11/2001	0.00	—	366	186
North Fork Cache Creek at Highway 20	1/11/2001	—	0.25	9.50	2.10
Sulphur Creek at Wilbur Springs	1/11/2001	0.37	—	3,070	318
Bear Creek above Holsten Chimney Canyon	2/13/2001	1.42	—	144	64.5
Bear Creek above Sulphur Creek	2/13/2001	—	0.11	1.70	1.00
Cache Creek near Lower Lake	2/13/2001	0.11	—	3.50	1.70
Cache Creek at Rumsey	2/13/2001	—	4.70	37.5	11.5
Cache Creek at Highway 505	2/13/2001	—	NA	19.9	4.40
Harley Gulch near Wilbur Springs	2/13/2001	0.00	—	169	92.8
North Fork Cache Creek at Highway 20	2/13/2001	—	0.91	2.6	1.60
Sulphur Creek at Wilbur Springs	2/13/2001	0.13	—	906	317
Bear Creek above Holsten Chimney Canyon	2/20/2001	5.18	—	150	43.5
Cache Creek near Lower Lake	2/20/2001	0.13	—	13.9	6.65
Harley Gulch near Wilbur Springs	2/20/2001	0.00	—	100	65.5
North Fork Cache Creek near Clearlake Oaks	2/20/2001	0.34	—	3.85	2.55
Sulphur Creek at Wilbur Springs	2/20/2001	0.59	—	685	310
Cache Creek at Rumsey	2/21/2001	—	28.60	60.5	11.1
North Fork Cache Creek at Highway 20	2/21/2001	—	7.93	17.4	7.15
Cache Creek out of Settling Basin	2/22/2001	26.40	—	53.5	12.2
Cache Creek Into Settling Basin	2/22/2001	26.40	—	58.5	9.45
Yolo Bypass at Interstate 80 near West Sacramento	2/22/2001	40.21	—	34.3	6.40
Lower Yolo Bypass	2/23/2001	40.21	—	36.8	4.70
Cache Creek at Rumsey	3/23/2001	4.02	—	5.25	2.16
Bear Creek above Holsten Chimney Canyon	3/23/2001	0.91	—	31.4	16
Bear Creek above Sulphur Creek	3/23/2001	NA	—	1.42	0.81

Appendix 1. Table 1. Stream discharge and concentrations of mercury in unfiltered and filtered water from sites in the Cache Creek Basin, California—*Continued*

Site	Date	Daily mean stream discharge, in m^3/s	Instantaneous stream discharge, in m^3/s	Mercury in unfiltered water, in ng/L	Mercury in filtered water, in ng/L
Cache Creek near Lower Lake	3/23/2001	0.18	—	8.82	2.25
North Fork Cache Creek at Highway 20	3/23/2001	1.48	—	2.31	1.22
Bear Creek above Holsten Chimney Canyon	5/3/2001	0.31	—	35.5	17.9
Bear Creek above Sulphur Creek	5/3/2001	NA	—	0.98	0.54
Cache Creek near Lower Lake	5/3/2001	0.31	—	2.53	0.63
Cache Creek at Rumsey	5/3/2001	NA	—	10	1.12
Harley Gulch near Wilbur Springs	5/3/2001	0.00	—	265	106
North Fork Cache Creek at Highway 20	5/3/2001	NA	—	5.09	0.80
Sulphur Creek at Wilbur Springs	5/3/2001	0.03	—	557	124

Appendix 1. Table 2. Stream discharge and concentrations of methylmercury in unfiltered and filtered water from sites in the Cache Creek Basin, California

[m^3/s, cubic meter per second; NA, not available; ng/L, nanogram per liter; —, not measured; <, less than indicated value]

Site	Date	Daily mean stream discharge, in m3/s	Instantaneous stream discharge, in m3/s	Methylmercury in unfiltered water, in ng/L	Methylmercury in filtered water, in ng/L
Bear Creek above Holsten Chimney Canyon	1/31/2000	4.00	—	0.58	0.48
Cache Creek at Rumsey	1/31/2000	—	5.40	0.78	0.23
Cache Creek into Settling Basin	1/31/2000	5.00	—	0.18	0.09
Cache Creek near Lower Lake	1/31/2000	0.15	—	0.11	0.11
Harley Gulch near Wilbur Springs	1/31/2000	0.13	—	0.98	0.63
North Fork Cache Creek at Highway 20	1/31/2000	—	4.40	0.17	0.22
Sulphur Creek at Wilbur Springs	1/31/2000	0.62	—	2.46	0.30
Bear Creek above Holsten Chimney Canyon	2/27/2000	16.60	—	0.30	0.18
Harley Gulch near Wilbur Springs	2/27/2000	0.21	—	0.07	0.12
Sulphur Creek at Wilbur Springs	2/27/2000	1.02	—	0.33	0.29
Cache Creek at Rumsey	2/28/2000	—	60.71	0.13	< 0.024
Davis Creek Reservoir at Dam	2/28/2000	1.90	—	0.33	0.16
North Fork Cache Creek at Highway 20	2/28/2000	—	63.01	0.08	< 0.023
Cache Creek near Lower Lake	2/29/2000	51.80	—	0.13	< 0.023
North Fork Cache Creek near Clearlake Oaks	2/29/2000	65.40	—	0.03	< 0.023
Cache Creek into Settling Basin	3/1/2000	139.00	—	0.58	< 0.023
Cache Creek out of Settling Basin	3/1/2000	139.00	—	0.44	< 0.023
Bear Creek above Holsten Chimney Canyon	3/2/2000	5.60	—	0.26	0.14
Bear Creek above Sulphur Creek	3/2/2000	—	4.20	0.10	0.02
Cache Creek at Rumsey	3/2/2000	—	116.70	0.22	0.02
Cache Creek into Settling Basin	3/2/2000	129.70	—	0.35	0.05
Cache Creek near Lower Lake	3/2/2000	52.70	—	0.15	0.07
Harley Gulch near Wilbur Springs	3/2/2000	0.04	—	0.12	0.10
North Fork Cache Creek at Highway 20	3/2/2000	—	75.50	0.07	0.02
Sulphur Creek at Wilbur Springs	3/2/2000	0.42	—	0.22	0.11
Yolo Bypass at Interstate 80 near West Sacramento	3/2/2000	1,283.26	—	0.20	0.03
Lower Yolo Bypass	3/3/2000	1,283.26	—	0.16	0.16
Davis Creek Reservoir at Dam	3/10/2000	1.36	—	0.27	0.10
Bear Creek above Holsten Chimney Canyon	3/15/2000	2.60	—	0.15	0.09
Harley Gulch near Wilbur Springs	3/15/2000	0.02	—	0.09	0.07
Sulphur Creek at Wilbur Springs	3/15/2000	0.18	—	0.06	< 0.023
Cache Creek at Rumsey	3/16/2000	—	43.72	0.07	< 0.023
Cache Creek at Rumsey	3/16/2000	—	43.20	0.10	0.07
Cache Creek at Highway 505	3/16/2000	—	51.00	0.15	0.07
Davis Creek Reservoir at Dam	3/16/2000	0.54	—	0.22	0.08
North Fork Cache Creek at Highway 20	3/16/2000	—	12.72	< 0.024	< 0.024
North Fork Cache Creek at Highway 20	3/16/2000	—	12.70	0.05	0.06
Cache Creek near Lower Lake	3/17/2000	5.90	—	0.05	< 0.023
North Fork Cache Creek near Clearlake Oaks	3/17/2000	7.70	—	< 0.023	< 0.023
Cache Creek into Settling Basin	3/18/2000	26.60	—	0.09	< 0.022
Cache Creek out of Settling Basin	3/18/2000	26.60	—	0.20	0.06
Yolo Bypass at Interstate 80 near West Sacramento	3/18/2000	96.32	—	0.48	0.17
Lower Yolo Bypass	3/22/2000	96.32	—	0.69	0.31
Bear Creek above Holsten Chimney Canyon	4/17/2000	2.12	—	0.35	0.16

Appendix 1. Table 2. Stream discharge and concentrations of methylmercury in unfiltered and filtered water from sites in the Cache Creek Basin, California—*Continued*

Site	Date	Daily mean stream discharge, in m3/s	Instantaneous stream discharge, in m3/s	Methylmercury in unfiltered water, in ng/L	Methylmercury in filtered water, in ng/L
Cache Creek at Rumsey	4/17/2000	—	54.40	0.41	0.04
Cache Creek into Settling Basin	4/17/2000	16.80	—	0.51	0.02
Cache Creek at Highway 505	4/17/2000	—	42.50	1.08	0.11
Cache Creek near Lower Lake	4/17/2000	28.30	—	0.47	0.13
Harley Gulch near Wilbur Springs	4/17/2000	0.05	—	0.45	0.41
North Fork Cache Creek at Highway 20	4/17/2000	—	4.10	0.02	0.02
Sulphur Creek at Wilbur Springs	4/17/2000	0.26	—	0.66	0.38
Cache Creek near Lower Lake	6/13/2000	19.70	—	0.12	0.03
Davis Ck above Davis Creek Reservoir	6/13/2000	0.01	—	0.36	0.18
Davis Creek Reservoir at Dam	6/13/2000	0.00	—	0.74	0.61
Harley Gulch near Wilbur Springs	6/13/2000	0.00	—	7.76	1.57
North Fork Cache Creek at Highway 20	6/13/2000	—	0.85	0.08	0.02
Bear Creek above Holsten Chimney Canyon	6/14/2000	0.09	—	0.17	0.13
Bear Creek above Sulphur Creek	6/14/2000	—	0.07	0.21	0.09
Cache Creek at Rumsey	6/14/2000	—	34.55	0.20	0.13
Cache Creek into Settling Basin	6/14/2000	1.70	—	0.26	0.09
Cache Creek at Highway 505	6/14/2000	—	0.85	0.27	0.08
Sulphur Creek at Wilbur Springs	6/14/2000	0.01	—	0.76	0.21
Bear Creek above Holsten Chimney Canyon	8/10/2000	0.04	—	1.09	0.15
Cache Creek at Rumsey	8/10/2000	—	14.70	0.23	0.10
Cache Creek into Settling Basin	8/10/2000	0.88	—	0.48	0.09
Cache Creek at Highway 505	8/10/2000	—	0.30	0.14	0.82
Cache Creek near Lower Lake	8/10/2000	15.60	—	0.18	0.02
Davis Ck above Davis Creek Reservoir	8/10/2000	0.00	—	0.24	0.17
North Fork Cache Creek at Highway 20	8/10/2000	—	0.30	0.19	0.03
Sulphur Creek at Wilbur Springs	8/10/2000	0.00	—	4.04	0.07
Bear Creek above Holsten Chimney Canyon	10/11/2000	0.10	—	0.13	0.13
Bear Creek above Sulphur Creek	10/11/2000	0.09	—	0.09	0.02
Cache Creek at Rumsey	10/11/2000	—	9.60	0.11	0.03
Cache Creek into Settling Basin	10/11/2000	2.40	—	0.18	0.07
Cache Creek at Highway 505	10/11/2000	1.00	—	0.19	0.05
Cache Creek near Lower Lake	10/11/2000	7.70	—	0.03	0.03
North Fork Cache Creek at Highway 20	10/11/2000	—	0.20	0.04	0.03
Sulphur Creek at Wilbur Springs	10/11/2000	0.01	ó	1.57	1.02
Bear Creek above Holsten Chimney Canyon	11/7/2000	—	0.09	0.32	0.28
Bear Creek above Sulphur Creek	11/7/2000	0.00	—	0.05	0.05
Cache Creek at Rumsey	11/7/2000	0.02	—	0.05	0.03
Cache Creek into Settling Basin	11/7/2000	—	0.57	0.09	0.04
Cache Creek at Highway 505	11/7/2000	0.09	—	0.07	0.03
Cache Creek near Lower Lake	11/7/2000	0.13	—	0.02	0.03
North Fork Cache Creek at Highway 20	11/7/2000	—	0.23	0.02	0.04
Sulphur Creek at Wilbur Springs	11/7/2000	—	0.00	1.30	1.31

Appendix 1. Table 2. Stream discharge and concentrations of methylmercury in unfiltered and filtered water from sites in the Cache Creek Basin, California—*Continued*

Site	Date	Daily mean stream discharge, in m3/s	Instantaneous stream discharge, in m3/s	Methylmercury in unfiltered water, in ng/L	Methylmercury in filtered water, in ng/L
Bear Creek above Holsten Chimney Canyon	12/11/2000	—	0.28	0.22	0.12
Bear Creek above Sulphur Creek	12/11/2000	0.11	—	0.07	0.03
Cache Creek at Rumsey	12/11/2000	—	0.07	0.04	0.04
Cache Creek at Highway 505	12/11/2000	0.11	—	0.09	0.03
Cache Creek near Lower Lake	12/11/2000	0.48	—	0.02	0.03
North Fork Cache Creek at Highway 20	12/11/2000	—	—	0.03	0.03
Bear Creek above Holsten Chimney Canyon	1/11/2001	—	0.28	0.47	0.13
Bear Creek above Sulphur Creek	1/11/2001	—	0.25	0.18	0.06
Cache Creek at Rumsey	1/11/2001	0.37	—	0.04	0.03
Cache Creek at Highway 505	1/11/2001	2.40	—	0.09	0.06
Cache Creek near Lower Lake	1/11/2001	—	0.99	0.05	0.02
Harley Gulch near Wilbur Springs	1/11/2001	0.14	—	1.09	0.45
North Fork Cache Creek at Highway 20	1/11/2001	—	—	0.06	0.04
Sulphur Creek at Wilbur Springs	1/11/2001	0.00	—	0.92	0.09
Bear Creek above Holsten Chimney Canyon	2/13/2001	—	0.11	0.71	0.53
Bear Creek above Sulphur Creek	2/13/2001	—	0.91	0.05	0.03
Cache Creek at Rumsey	2/13/2001	0.13	—	0.28	0.12
Cache Creek at Highway 505	2/13/2001	1.42	—	0.23	0.09
Cache Creek near Lower Lake	2/13/2001	—	1.93	0.09	0.05
Harley Gulch near Wilbur Springs	2/13/2001	0.11	—	0.66	0.39
North Fork Cache Creek at Highway 20	2/13/2001	—	—	0.05	0.05
Sulphur Creek at Wilbur Springs	2/13/2001	0.00	—	0.41	0.13
Bear Creek above Holsten Chimney Canyon	2/20/2001	—	NA	0.67	0.44
Cache Creek near Lower Lake	2/20/2001	0.34	—	0.09	0.05
Harley Gulch near Wilbur Springs Cr	2/20/2001	—	—	0.39	0.29
North Fork. Cache Creek near Clearlake Oaks	2/20/2001	5.18	—	< 0.013	0.02
Sulphur Creek at Wilbur Springs	2/20/2001	0.00	—	0.49	0.43
Cache Creek at Rumsey	2/21/2001	—	7.93	0.59	0.13
North Fork Cache Creek at Highway 20	2/21/2001	0.59	—	0.17	0.07
Cache Creek out of Settling Basin	2/22/2001	40.21	—	0.33	0.17
Cache Creek into Settling Basin	2/22/2001	40.21	—	0.49	0.15
Cache Creek into Settling Basin (replicate)	2/22/2001	—	28.60	0.46	0.12
Yolo Bypass at Interstate 80 near West Sacramento	2/22/2001	26.40	—	0.35	0.11
Lower Yolo Bypass	2/23/2001	0.13	—	0.21	0.11
North Fork Cache Creek at Highway 20	3/15/2001	NA	—	0.07	0.02
Cache Creek at Rumsey	3/19/2001	1.48	—	0.10	0.02
Bear Creek above Holsten Chimney Canyon	3/23/2001	NA	—	0.30	0.09
Bear Creek above Sulphur Creek	3/23/2001	—	—	0.07	0.03
Cache Creek near Lower Lake	3/23/2001	0.91	—	0.15	0.03
North Fork Cache Creek at Highway 20	3/23/2001	0.18	—	0.09	0.04
Bear Creek above Holsten Chimney Canyon	5/3/2001	0.31	—	0.10	0.02

Appendix 1. Table 2. Stream discharge and concentrations of methylmercury in unfiltered and filtered water from sites in the Cache Creek Basin, California—*Continued*

Site	Date	Daily mean stream discharge, in m3/s	Instantaneous stream discharge, in m3/s	Methylmercury in unfiltered water, in ng/L	Methylmercury in filtered water, in ng/L
Bear Creek above Sulphur Creek	5/3/2001	NA	—	0.06	0.04
Cache Creek near Lower Lake	5/3/2001	0.31	—	0.26	0.08
Cache Creek at Rumsey	5/3/2001	NA	—	0.30	0.05
Harley Gulch near Wilbur Springs	5/3/2001	0.00	—	8.26	7.05
Sulphur Creek at Wilbur Springs	5/3/2001	0.03	—	0.15	0.81

Appendix 1. Table 3. Concentrations of mercury in unfiltered and filtered water, in field blanks, from sites in the Cache Creek Basin, California

[ng/L, nanogram per liter; <, less than indicated value]

Site	Date	Mercury in unfiltered water, in ng/L	Mercury in filtered water, in ng/L
Sulphur Creek at Wilbur Springs	2/27/2000	< 0.5	< 0.5
North Fork Cache Creek at Highway 20	2/28/2000	1.1	< 0.4
Harley Gulch near Wilbur Springs	2/27/2000	0.6	< 0.4
Sulphur Creek at Wilbur Springs	3/14/2000	< 0.5	< 0.5
Cache Creek at Rumsey	3/16/2000	< 0.5	< 0.5
North Fork Cache Creek at Highway 20	3/18/2000	0.6	0.7
Sulphur Creek at Wilbur Springs	2/20/2001	0.6	0.3
North Fork Cache Creek at Highway 20	2/21/2001	1.2	1.2

Appendix 1. Table 4. Concentrations of methylmercury in unfiltered and filtered water, in field blanks, from sites in the Cache Creek Basin, California

[ng/L, nanogram per liter; < , less than indicated value]

Site	Date	Methylmercury in unfiltered water, in ng/L	Methylmercury in filtered water, in ng/L
Sulphur Creek at Wilbur Springs	2/27/2000	< 0.021	< 0.023
North Fork Cache Creek at Highway 20	2/28/2000	0.022	0.020
Cache Creek near Lower Lake	3/17/2000	< 0.023	< 0.023
Cache Creek into Settling Basin	3/18/2000	< 0.022	< 0.023
Sulphur Creek at Wilbur Springs	2/20/2001	0.042	0.020
North Fork Cache Creek at Highway 20	2/21/2001	0.032	< 0.013

Appendix 1. Table 5. Replicate concentrations of mercury in unfiltered water from sites in the Cache Creek Basin, California

[ng/L, nanogram per liter]

Site	Date	Time	Replicate	Mercury in unfiltered water, in ng/L
Bear Creek above Holsten Chimney Canyon	2/27/2000	1115	1 of 2	217
Bear Creek above Holsten Chimney Canyon	2/27/2000	1115	2 of 2	172
Sulphur Creek at Wilbur Springs	2/27/2000	1400	1 of 2	547
Sulphur Creek at Wilbur Springs	2/27/2000	1400	2 of 2	537
Harley Gulch near Wilbur Springs	2/27/2000	1600	1 of 2	237
Harley Gulch near Wilbur Springs	2/27/2000	1600	2 of 2	249
North Fork Cache Creek at Highway 20	2/28/2000	945	1 of 2	24.3
North Fork Cache Creek at Highway 20	2/28/2000	945	2 of 2	23.1
Cache Creek at Rumsey	2/28/2000	1425	1 of 2	40.5
Cache Creek at Rumsey	2/28/2000	1425	2 of 2	40.7
Davis Creek Reservoir at Dam, near Knoxville	2/28/2000	1600	1 of 2	34.3
Davis Creek Reservoir at Dam, near Knoxville	2/28/2000	1600	2 of 2	31.7
Cache Creek near Lower Lake	2/29/2000	920	1 of 2	17.8
Cache Creek near Lower Lake	2/29/2000	920	2 of 2	17.2
North Fork Cache Creek near Clearlake Oaks	2/29/2000	1350	1 of 2	6.3
North Fork Cache Creek near Clearlake Oaks	2/29/2000	1350	2 of 2	4.1
Cache Creek into Settling Basin	3/1/2000	930	1 of 2	220
Cache Creek into Settling Basin	3/1/2000	930	2 of 2	197
Cache Creek out of Settling Basin	3/1/2000	1140	1 of 2	155
Cache Creek out of Settling Basin	3/1/2000	1140	2 of 2	166
Yolo Bypass at Interstate 80 near West Sacramento	3/2/2000	1200	1 of 2	20.6
Yolo Bypass at Interstate 80 near West Sacramento	3/2/2000	1200	2 of 2	20.3
Lower Yolo Bypass	3/3/2000	1350	1 of 2	14.4
Lower Yolo Bypass	3/3/2000	1550	2 of 2	12.7
Bear Creek above Holsten Chimney Canyon	3/15/2000	1220	1 of 2	32.0
Bear Creek above Holsten Chimney Canyon	3/15/2000	1220	2 of 2	33.5
Sulphur Creek at Wilbur Springs	3/15/2000	1550	1 of 2	536
Sulphur Creek at Wilbur Springs	3/15/2000	1550	2 of 2	520
Harley Gulch near Wilbur Springs	3/15/2000	1750	1 of 2	142
Harley Gulch near Wilbur Springs	3/15/2000	1750	2 of 2	146
North Fork Cache Creek at Highway 20	3/16/2000	1030	1 of 2	5.0
North Fork Cache Creek at Highway 20	3/16/2000	1030	2 of 2	5.1
Davis Creek Reservoir at Dam, near Knoxville	3/16/2000	1630	1 of 2	9.1
Davis Creek Reservoir at Dam, near Knoxville	3/16/2000	1630	2 of 2	10.2
North Fork Cache Creek near Clearlake Oaks	3/17/2000	1400	1 of 2	3.9
North Fork Cache Creek near Clearlake Oaks	3/17/2000	1400	2 of 2	3.0
Cache Creek into Settling Basin	3/18/2000	830	1 of 2	24.3
Cache Creek into Settling Basin	3/18/2000	830	2 of 2	24.2
Cache Creek out of Settling Basin	3/18/2000	1050	1 of 2	11.2
Cache Creek out of Settling Basin	3/18/2000	1050	2 of 2	11.2
Yolo Bypass at Interstate 80 near West Sacramento	3/18/2000	1300	1 of 2	15.5
Yolo Bypass at Interstate 80 near West Sacramento	3/18/2000	1300	2 of 2	15.9
Lower Yolo Bypass	3/22/2000	1110	1 of 2	39.4

Appendix 1. Table 5. Replicate concentrations of mercury in unfiltered water from sites in the Cache Creek Basin, California—*Continued*

[ng/L, nanogram per liter]

Site	Date	Time	Replicate	Mercury in unfiltered water, in ng/L
Lower Yolo Bypass	3/22/2000	1110	2 of 2	38.9
Bear Creek above Holsten Chimney Canyon	2/20/2001	1200	1 of 2	150
Bear Creek above Holsten Chimney Canyon	2/20/2001	1200	2 of 2	150
Harley Gulch near Wilbur Springs	2/20/2001	1340	2 of 2	100
Harley Gulch near Wilbur Springs	2/20/2001	1340	1 of 2	100
North Fork Cache Creek near Clearlake Oaks	2/20/2001	1400	1 of 2	3.9
North Fork Cache Creek near Clearlake Oaks	2/20/2001	1400	2 of 2	3.8
Sulphur Creek at Wilbur Springs	2/20/2001	1500	1 of 2	700
Sulphur Creek at Wilbur Springs	2/20/2001	1500	2 of 2	670
Cache Creek near Lower Lake	2/20/2001	1600	1 of 2	13.8
Cache Creek near Lower Lake	2/20/2001	1600	2 of 2	13.9
North Fork Cache Creek at Highway 20	2/21/2001	930	1 of 2	16.5
North Fork Cache Creek at Highway 20	2/21/2001	930	2 of 2	18.2
Cache Creek at Rumsey	2/21/2001	1220	1 of 2	63
Cache Creek at Rumsey	2/21/2001	1220	2 of 2	58
Cache Creek into Setting Basin	2/22/2001	1020	1 of 2	58
Cache Creek into Settling Basin	2/22/2001	1020	2 of 2	59
Cache Creek out of Setting Basin	2/22/2001	1050	1 of 2	48
Cache Creek out of Settling Basin	2/22/2001	1050	2 of 2	59
Yolo Bypass at Interstate 80 near West Sacramento	2/22/2001	1240	1 of 2	34.1
Yolo Bypass at Interstate 80 near West Sacramento	2/22/2001	1240	2 of 2	34.5
Lower Yolo Bypass	2/23/2001	1100	1 of 2	18.2
Lower Yolo bypass	2/23/2001	1100	2 of 2	55.3

Appendix 1. Table 6. Replicate concentrations of mercury in filtered water from sites in the Cache Creek Basin, California

[ng/L, nanogram per liter]

Site	Date	Time	Replicate	Mercury in filtered water, in ng/L
Sulphur Creek at Wilbur Springs	2/27/2000	1400	1 of 2	316
Sulphur Creek at Wilbur Springs	2/27/2000	1400	2 of 2	334
Sulphur Creek at Wilbur Springs	2/27/2000	1401	1 of 2	322
Sulphur Creek at Wilbur Springs	2/27/2000	1401	2 of 2	258
Harley Gulch near Wilbur Springs	2/27/2000	1600	1 of 2	58
Harley Gulch near Wilbur Springs	2/27/2000	1600	2 of 2	62
Bear Creek above Holsten Chimney Canyon	2/27/2000	1115	1 of 2	22.4
Bear Creek above Holsten Chimney Canyon	2/27/2000	1115	2 of 2	24.1
North Fork Cache Creek at Highway 20	2/28/2000	945	1 of 2	2.1
North Fork Cache Creek at Highway 20	2/28/2000	945	2 of 2	1.7
Cache Creek at Rumsey	2/28/2000	1425	1 of 2	4.1
Cache Creek at Rumsey	2/28/2000	1425	2 of 2	3.4
Cache Creek at Rumsey	2/28/2000	1426	1 of 2	3.2
Cache Creek at Rumsey	2/28/2000	1426	2 of 2	3.5
Davis Creek Reservoir at Dam, near Knoxville	2/28/2000	1600	1 of 2	6.5
Davis Creek Reservoir at Dam, near Knoxville	2/28/2000	1600	2 of 2	6.7
North Fork Cache Creek near Clearlake Oaks	2/29/2000	1350	1 of 2	1.9
North Fork Cache Creek near Clearlake Oaks	2/29/2000	1350	2 of 2	1.8
Cache Creek out of Settling basin	3/1/2000	1140	1 of 2	5.0
Cache Creek out of Settling basin	3/1/2000	1140	2 of 2	4.4
Yolo Bypass at Interstate 80 near West Sacramento	3/2/2000	1200	1 of 2	1.9
Yolo Bypass at Interstate 80 near West Sacramento	3/2/2000	1200	2 of 2	2.2
Lower Yolo Bypass	3/3/2000	1350	1 of 2	3.4
Lower Yolo Bypass	3/3/2000	1350	2 of 2	3.3
Sulphur Creek at Wilbur Springs	3/15/2000	1550	1 of 2	353
Sulphur Creek at Wilbur Springs	3/15/2000	1550	2 of 2	331
Harley Gulch near Wilbur Springs	3/15/2000	1750	1 of 2	69
Harley Gulch near Wilbur Springs	3/15/2000	1750	2 of 2	70
Bear Creek above Holsten Chimney Canyon	3/15/2000	1220	1 of 2	12.3
Bear Creek above Holsten Chimney Canyon	3/15/2000	1220	2 of 2	12.5
North Fork Cache Creek at Highway 20	3/16/2000	1030	1 of 2	0.9
North Fork Cache Creek at Highway 20	3/16/2000	1030	2 0f 2	0.8
Cache Creek at Rumsey	3/16/2000	1350	1 of 2	2.0
Cache Creek at Rumsey	3/16/2000	1350	2 of 2	1.5
Davis Creek Reservoir at Dam, near Knoxville	3/16/2000	1630	1 of 2	4.2
Davis Creek Reservoir at Dam, near Knoxville	3/16/2000	1630	2 of 2	3.7
North Fork Cache Creek near Clearlake Oaks	3/17/2000	1400	1 of 2	2.0
North Fork Cache Creek near Clearlake Oaks	3/17/2000	1400	2 of 2	4.1
Cache Creek near Lower Lake	3/17/2000	940	1 of 2	2.5
Cache Creek near Lower Lake	3/17/2000	940	2 of 2	3.4
Cache Creek into Settling Basin	3/18/2000	830	1 of 2	1.5

Appendix 1. Table 6. Replicate concentrations of mercury in filtered water from sites in the Cache Creek Basin, California—*Continued*

[ng/L, nanogram per liter]

Site	Date	Time	Replicate	Mercury in filtered water, in ng/L
Cache Creek into Settling Basin	3/18/2000	830	2 of 2	1.5
Cache Creek out of Settling Basin	3/18/2000	1050	1 of 2	1.6
Cache Creek out of Settling Basin	3/18/2000	1050	2 of 2	1.6
Yolo Bypass at Interstate 80 near West Sacramento	3/18/2000	1300	1 of 2	1.5
Yolo Bypass at Interstate 80 near West Sacramento	3/18/2000	1300	2 of 2	1.8
Lower Yolo Bypass	3/22/2000	1110	1 of 2	1.8
Lower Yolo Bypass	3/22/2000	1110	2 of 2	1.7
Bear Creek above Holsten Chimney Canyon	2/20/2001	1200	1 of 2	42
Bear Creek above Holsten Chimney Canyon	2/20/2001	1200	2 of 2	45
Harley Gulch near Wilbur Springs	2/20/2001	1340	1 of 2	67
Harley Gulch near Wilbur Springs	2/20/2001	1340	2 of 2	64
North Fork Cache Creek near Clearlake Oaks	2/20/2001	1400	2 of 2	2.6
North Fork Cache Creek near Clearlake Oaks	2/20/2001	1400	1 of 2	2.5
Sulphur Creek at Wilbur Springs	2/20/2001	1500	1 of 2	290
Sulphur Creek at Wilbur Springs	2/20/2001	1500	2 of 2	330
Cache Creek near Lower Lake	2/20/2001	1600	1 of 2	6.5
Cache Creek near Lower Lake	2/20/2001	1600	2 of 2	6.8
Cache Creek at Rumsey	2/21/2001	1220	1 of 2	11.5
Cache Creek at Rumsey	2/21/2001	1220	2 of 2	10.7
North Fork Cache Creek at Highway 20	2/21/2001	930	2 of 2	7.1
North Fork Cache Creek at Highway 20	2/21/2001	930	1 of 2	7.2
Cache Creek into Settling Basin	2/21/2001	1020	1 of 2	9.5
Cache Creek into Settling Basin	2/21/2201	1020	2 of 2	9.4
Cache Creek out of Settling Basin	2/21/2001	1050	1 of 2	11.8
Cache Creek out of Settling Basin	2/21/2201	1050	2 of 2	12.5
Yolo Bypass at Interstate 80 near West Sacramento	2/22/2001	1240	1 of 2	6.5
Yolo Bypass at Interstate 80 near West Sacramento	2/22/2001	1240	2 of 2	6.3
Lower Yolo Bypass	2/23/2001	1100	1 of 2	4.6
Lower Yolo Bypass	2/23/2001	1100	2 of 2	4.8

Appendix 1. Table 7. Replicate concentrations of methylmercury in unfiltered water from sites in the Cache Creek Basin, California

[ng/L, nanogram per liter]

Site	Date	Time	Replicate	Methylmercury in unfiltered water, in ng/L
Cache Creek at Rumsey	2/28/2000	1425	1 of 2	0.14
Cache Creek at Rumsey	2/28/2000	1425	2 of 2	0.13
Sulphur Creek at Wilbur Springs	2/29/2000	1400	1 of 2	0.33
Sulphur Creek at Wilbur Springs	2/29/2000	1400	2 of 2	0.30
Bear Creek near Holsten Chimney Canyon	3/15/2000	1220	1 of 2	0.15
Bear Creek near Holsten Chimney Canyon	3/15/2000	1220	2 of 2	0.19
Cache Creek near Lower Lake	3/17/2000	940	1 of 2	0.048
Cache Creek near Lower Lake	3/17/2000	940	2 of 2	0.049
North Fork Cache Creek at Highway 20	2/21/2001	930	1 of 2	0.17
North Fork Cache Creek at Highway 20	2/21/2001	930	2 of 2	0.14
Cache Creek into Settling Basin	2/22/2001	1020	1 of 2	0.49
Cache Creek into Settling Basin	2/22/2001	1020	2 of 2	0.46

Appendix 1. Table 8. Replicate concentrations of methylmercury in filtered water from sites in the Cache Creek Basin, California

[ng/L, nanogram per liter; <, less than indicated value]

Site	Date	Time	Replicate	Methylmercury in filtered water, in ng/L
Cache Creek at Rumsey	2/28/2000	1425	1 of 2	< 0.024
Cache Creek at Rumsey	2/28/2000	1425	2 of 2	< 0.024
Sulphur Creek at Wilbur Springs	2/29/2000	1400	1 of 2	0.29
Sulphur Creek at Wilbur Springs	2/29/2000	1400	2 of 2	0.30
Bear Creek near Holsten Chimney Canyon	3/15/2000	1220	1 of 2	0.095
Bear Creek near Holsten Chimney Canyon	3/15/2000	1220	2 of 2	0.19
Cache Creek near Lower Lake	3/17/2000	940	1 of 2	< 0.023
Cache Creek near Lower Lake	3/17/2000	940	2 of 2	< 0.023
North Fork Cache Creek at Highway 20	2/21/2001	930	1 of 2	0.073
North Fork Cache Creek at Highway 20	2/21/2001	930	2 of 2	0.078
Cache Creek into Settling Basin	2/22/2001	1020	1 of 2	0.15
Cache Creek into Settling Basin	2/22/2001	1020	2 of 2	0.12

Appendix 1. Table 9. Stable isotopes in water from sites in Cache Creek Basin, California

[$\delta^{18}O$, delta oxygen-18; δD, delta deuterium; per mil, per thousand; VSMOW, Vienna Standard Mean Ocean Water; NA, not available;]

Date	Time	Site	$\delta^{18}O$ (per mil, VSMOW)	δD (per mil, VSMOW)
7/21/1999	1230	Cache Creek at Rumsey	−5.84	−45.8
8/18/1999	1100	Cache Creek at Rumsey	−4.27	−38.3
2/27/2000	1115	Bear Creek above Holsten Chimney Canyon	−9.38	−68.9
2/27/2000	1400	Sulfur Creek at Wilbur Springs	−9.43	−69.3
2/27/2000	1600	Harley Gulch near Wilbur Springs	−9.30	−69.1
2/28/2000	945	North Fork Cache Creek at Highway 20	−7.93	−57.7
2/28/2000	1425	Cache Creek at Rumsey	−8.18	−59.8
2/28/2000	1600	Davis Creek Reservoir at Dam, near Knoxville	−6.55	−51.4
2/29/2000	920	Cache Creek near Lower Lake	−7.02	−54.8
2/29/2000	1350	North Fork Cache Creek at Highway 20	−7.42	−56.0
3/1/2000	930	Cache Creek into Settling Basin	−7.68	−57.5
3/1/2000	1140	Cache Creek out of Settling Basin	−7.72	−57.8
3/2/2000	1200	Yolo Bypass at Interstate 80 near West Sacramento	−10.41	−76.7
3/3/2000	1350	Lower Yolo Bypass	−11.04	−78.7
3/15/2000	1220	Bear Creek above Holsten Chimney Canyon	−8.56	−63.4
3/15/2000	1550	Sulfur Creek at Wilbur Springs	−7.84	−60.9
3/15/2000	1750	Harley Gulch near Wilbur Springs	−8.14	−61.8
3/16/2000	1030	North Fork Cache Creek at Highway 20	−7.91	−57.6
3/16/2000	1350	Cache Creek at Rumsey	−6.29	−49.4
3/17/2000	940	Cache Creek near Lower Lake	−4.42	−38.2
3/17/2000	1400	North Fork Cache Creek near Clearlake Oaks	−7.52	−56.4
3/18/2000	830	Cache Creek into Settling Basin	−6.82	−51.3
3/18/2000	1050	Cache Creek out of Settling Basin	−6.24	−47.5
3/18/2000	1300	Yolo Bypass at Interstate 80 near West Sacramento	−8.78	−67.2
3/22/2000	1110	Lower Yolo Bypass	−7.86	−60.4
4/17/2000	1200	Cache Creek near Lower Lake	−4.88	−42.4
4/17/2000	1200	Cache Creek into Settling Basin	−7.44	−57.1
4/17/2000	1200	Cache Creek at Rumsey	−6.01	−47.1
4/17/2000	1200	Bear Creek above Holsten Chimney Canyon	−8.07	−61.8
4/17/2000	1200	North Fork Cache Creek at Highway 20	−8.40	−59.7
4/17/2000	1200	Harley Gulch near Wilbur Springs	−8.18	−60.4
6/13/2000	1200	Cache Creek near Lower Lake	−4.25	−35.7
6/13/2000	1200	Davis Creek Reservoir at Dam, near Knoxville	−7.58	−53.3
6/13/2000	1200	North Fork Cache Creek at Highway 20	−7.67	−56.5
6/13/2000	1200	Harley Gulch near Wilbur Springs	−6.94	−56.2
6/14/2000	1200	Cache Creek at Rumsey	−4.81	−40.2
6/14/2000	1200	Bear Creek above Holsten Chimney Canyon	−6.87	−56.6
6/14/2000	1200	Bear Creek above Sulphur Creek	−7.74	−58.8
6/14/2000	1200	Sulfur Creek at Wilbur Springs	−2.33	−40.4
6/14/2000	1200	Cache Creek into Settling Basin	−4.70	−41.2

Appendix 1. Table 9. Stable isotopes in water from sites in Cache Creek Basin, California—*Continued*

[$\delta^{18}O$, delta oxygen-18; δD, delta deuterium; per mil, per thousand; VSMOW, Vienna Standard Mean Ocean Water; NA, not available;]

Date	Time	Site	$\delta^{18}O$ (per mil, VSMOW)	δD (per mil, VSMOW)
6/14/2000	1200	Cache Creek at Highway 505	–4.75	–43.1
8/10/2000	1040	Davis Creek Reservoir at Dam, near Knoxville	–7.42	–53.2
8/10/2000	1155	Cache Creek near Lower Lake	–3.75	–35.3
8/10/2000	1240	North Fork Cache Creek at Highway 20	–7.27	–54.8
8/10/2000	1325	Sulfur Creek at Wilbur Springs	4.00	–20.7
8/10/2000	1350	Bear Creek above Holsten Chimney Canyon	–4.73	–48.0
8/10/2000	1430	Cache Creek at Rumsey	–3.70	–35.6
8/10/2000	1530	Cache Creek at Highway 505	–5.07	–43.4
8/10/2000	1610	Cache Creek into Settling Basin	–4.11	–38.7
10/11/2000	1445	Cache Creek near Lower Lake	–3.16	–33.1
10/11/2000	1230	North Fork Cache Creek at Highway 20	–7.32	–54.7
10/11/2000	1320	Bear Creek above Sulphur Creek	–7.78	–60.2
10/11/2000	1420	Bear Creek above Holsten Chimney Canyon	–5.90	–52.3
10/11/2000	1500	Cache Creek at Rumsey	–3.34	–32.3
10/11/2000	1605	Cache Creek at Highway 505	–3.80	–33.9
10/11/2000	1645	Cache Creek into Settling Basin	–3.83	–33.2
10/11/2000	1200	Sulfur Creek at Wilbur Springs	1.94	–28.4
11/6/2000	1400	Davis Creek below Davis Creek Reservoir	–5.66	–46.1
11/6/2000	1500	Davis Creek Reservoir at Dam, near Knoxville	–7.49	–53.4
11/7/2000	1000	Cache Creek near Lower Lake	–3.01	–33.8
11/7/2000	1115	North Fork Cache Creek at Highway 20	–7.49	–57.1
11/7/2000	1210	Bear Creek above Sulphur Creek	–7.78	–59.2
11/7/2000	1245	Sulfur Creek at Wilbur Springs	–0.07	–33.7
11/7/2000	1315	Bear Creek above Holsten Chimney Canyon	–6.31	–53.5
11/7/2000	1355	Cache Creek at Rumsey	–6.00	–49.1
11/7/2000	1500	Cache Creek at Highway 505	–5.16	–44.3
11/7/2000	1600	Cache Creek into Settling Basin	–5.12	–44.4
12/11/2000	1100	Cache Creek near Lower Lake	–3.12	–33.0
12/11/2000	1215	North Fork Cache Creek at Highway 20	–7.48	–54.3
12/11/2000	1310	Bear Creek above Sulphur Creek	–8.01	–59.6
12/11/2000	1200	Bear Creek above Holsten Chimney Canyon	–6.62	–56.6
12/11/2000	1200	Cache Creek at Highway 505	–5.37	–45.6
12/11/2000	1200	Cache Creek at Rumsey	–6.26	–51.0
1/11/2001	1055	Cache Creek near Lower Lake	–4.20	–40.2
1/11/2001	1205	North Fork Cache Creek at Highway 20	–7.88	–59.2
1/11/2001	1245	Harley Gulch near Wilbur Springs	–7.40	–56.7
1/11/2001	1320	Bear Creek above Sulphur Creek	–6.88	–61.7
1/11/2001	1405	Sulfur Creek at Wilbur Springs	–6.96	–56.4
1/11/2001	1445	Bear Creek above Holsten Chimney Canyon	–8.01	–60.1
1/11/2001	1525	Cache Creek at Rumsey	–7.07	–52.0

Appendix 1. Table 9. Stable isotopes in water from sites in Cache Creek Basin, California—*Continued*

[$\delta^{18}O$, delta oxygen-18; δD, delta deuterium; per mil, per thousand; VSMOW, Vienna Standard Mean Ocean Water; NA, not available;]

Date	Time	Site	$\delta^{18}O$ (per mil, VSMOW)	δD (per mil, VSMOW)
1/11/2001	1625	Cache Creek at Highway 505	–6.09	–49.7
2/13/2001	925	Cache Creek at Highway 505	–8.15	–59.5
2/13/2001	1200	North Fork Cache Creek at Highway 20	–8.05	–60.0
2/13/2001	1140	Cache Creek near Lower Lake	–6.00	–46.8
2/13/2001	1400	Cache Creek at Rumsey	–8.60	–62.1
2/13/2001	1410	Harley Gulch near Wilbur Springs	–8.35	–61.6
2/13/2001	1445	Bear Creek above Sulphur Creek	–8.82	–63.7
2/13/2001	1505	Sulfur Creek at Wilbur Springs	–7.24	–59.3
2/13/2001	1535	Bear Creek above Holsten Chimney Canyon	–9.07	–67.0
2/13/2001	1600	Cache Creek at Rumsey	–8.61	–62.6
2/20/2001	1200	Bear Creek above Holsten Chimney Canyon	–8.88	–63.6
2/20/2001	1340	Harley Gulch near Wilbur Springs	–8.84	–62.4
2/20/2001	14;00	North Fork Cache Creek near Clear Lake Oak	–6.85	–53.9
2/20/2001	1500	Sulfur Creek at Wilbur Springs	–8.74	–62.9
2/20/2001	1600	Cache Creek near Lower Lake	–7.04	–51.3
2/21/2001	930	North Fork Cache Creek at Highway 20	–9.05	–62.2
2/21/2001	1220	Cache Creek at Rumsey	–8.86	–60.3
2/22/2001	1016	Sulfur Creek at Wilbur Springs	–8.27	–58.4
2/22/2001	1020	Cache Creek into Settling Basin	–8.53	–58.5
2/22/2001	1040	Sulfur Creek Mine	–8.05	–59.2
2/22/2001	1050	Cache Creek out of Settling Basin	–8.46	–59.1
2/22/2001	1145	Sulfur Creek Mine	4.79	–21.9
2/22/2001	1155	Sulfur Creek Mine	4.78	–20.9
2/22/2001	1215	Sulfur Creek Mine	4.66	–19.4
2/22/2001	1240	Yolo Bypass at Interstate 80 near West Sacramento	–7.72	–56.8
2/22/2001	1318	Sulfur Creek Mine	–8.55	–59.5
2/22/2001	1335	Sulfur Creek Mine	6.17	–14.1
2/22/2001	1455	Abbott and Turkey Run Mines	–8.91	–64.1
2/22/2001	1503	Sulfur Creek Mine	–5.60	–50.7
2/22/2001	1520	Sulfur Creek Mine	–8.26	–57.9
2/22/2001	1613	Sulfur Creek Mine	–8.74	–59.9
2/23/2001	1100	Lower Yolo Bypass	–8.47	–63.2
3/22/2001	1045	Cache Creek near Lower Lake	–8.69	–61.1
3/22/2001	1145	North Fork Cache Creek at Highway 20	–8.58	–59.7
3/22/2001	1245	Bear Creek above Sulphur Creek	–8.81	–64.4
3/22/2001	1415	Bear Creek above Holsten Chimney Canyon	–8.31	–61.2
3/22/2001	NA	Cache Creek at Rumsey	–8.22	–61.6
5/3/2001	1140	North Fork Cache Creek at Highway 20	–7.07	–53.5
5/3/2001	1205	Harley Gulch near Wilbur Springs	–7.12	–55.0
5/3/2001	1245	Bear Creek above Sulphur Creek	–7.78	–57.7
5/3/2001	1340	Sulfur Creek at Wilbur Springs	–2.77	–42.9
5/3/2001	1410	Bear Creek above Holsten Chimney Canyon	–6.61	–54.8

Appendix 1. Table 9. Stable isotopes in water from sites in Cache Creek Basin, California—*Continued*

[$\delta^{18}O$, delta oxygen-18; δD, delta deuterium; per mil, per thousand; VSMOW, Vienna Standard Mean Ocean Water; NA, not available;]

Date	Time	Site	$\delta^{18}O$ (per mil, VSMOW)	δD (per mil, VSMOW)
5/3/2001	1545	Cache Creek at Rumsey	–7.02	–53.4
2/21/2001	1050	Abbott and Turkey Run Mines	–8.77	–50.8
2/21/2001	1107	Abbott and Turkey Run Mines	–7.73	–50.8
2/21/2001	1305	Abbott and Turkey Run Mines	–5.91	–50.8
2/21/2001	1345	Abbott and Turkey Run Mines	–8.56	–50.8
2/21/2001	1100	Davis Creek Resrvoir at Dam, near Knoxville	–6.86	–50.8